



Chapter 3

Chemical Equilibrium

3.1 The Equilibrium Constant

OBJECTIVES

After studying this topic, you should be able to:

- Write an equilibrium constant expression (K) for a given chemical equilibrium and vice versa.
- Determine equilibrium concentrations of reactants and products for an equilibrium, given the K value and vice versa.
- Determine the reaction quotient (Q) and the direction in which a reaction will proceed to achieve equilibrium.
- Describe Le Châtelier's principle, and apply the principle to determine the direction a reaction will shift when subjected to a stress.
- Identify the relationship between the Gibbs free energy (ΔG°) and K , and use this relationship to determine the standard enthalpy and entropy of a reaction (ΔH_{rxn}° and ΔS_{rxn}°).
- Describe and apply the van't Hoff relationship between K and temperature.

INTRODUCTION

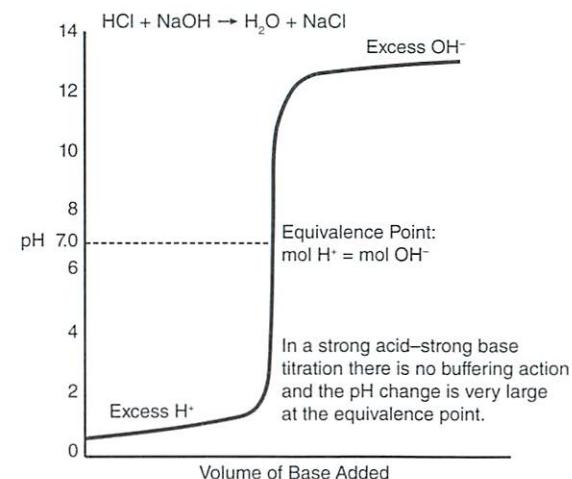
So far, the study of chemical reactions has focused on reactions that proceed in one direction, to completion. The amount of product made, or reagent remaining, was determined using the limiting reagent. However, there are many chemical reactions that are reversible. When these reactions are complete (have reached equilibrium), the system contains both reactants and products.

We may fairly judge the commercial prosperity of a country by the amount of sulfuric acid it consumes.

Justus Von Liebig (1803–1873)

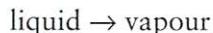
Topics Covered:

- 3.1 The Equilibrium Constant
- 3.2 Solubility of Ionic Compounds
- 3.3 Weak Acids and Bases
- 3.4 Buffer Solutions

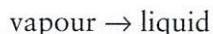


WHAT IS EQUILIBRIUM?

If a container is half-filled with water and then sealed, some, but not all, of the liquid water molecules will vapourize:



After some length of time, there will be sufficient water vapour that the reverse reaction can also occur:



At some point, the number of liquid and gaseous water molecules in the system (the sealed flask) becomes constant. At this stage, the system is said to have reached or established *equilibrium*. This process is written as:



Although the number of liquid and gaseous molecules remains constant at equilibrium, there is in fact a great deal of liquid-to-gas and gas-to-liquid conversion taking place (see Figure 3.1.1). Therefore, a system that is at equilibrium is dynamic and not static. The liquid will continue to evaporate, and the gas will continue to condense.

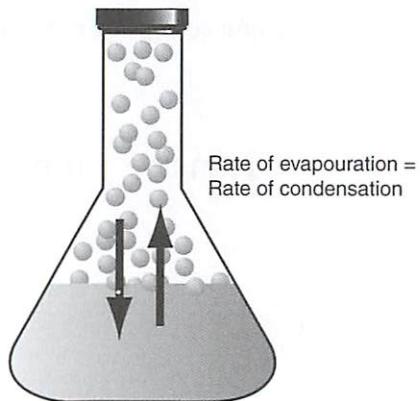


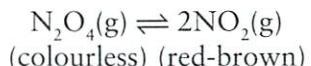
Figure 3.1.1 $\text{H}_2\text{O}(g)$ in equilibrium with $\text{H}_2\text{O}(l)$.

Figure 3.1.1 shows an equilibrium involving physical states, but the same principles can be applied to chemical processes.



In chemical processes, equilibrium is defined as the condition where the rate of the forward reaction is equal to the rate of the reverse reaction.

For example, what happens when a system at equilibrium involves the type of reaction shown in the following equation?



If the system initially contains only N_2O_4 , then the system is colourless. As the reaction proceeds, a red-brown colour is seen (NO_2 gas). When the system reaches equilibrium, the colour of the gas mixture is yellow and there are measurable amounts of both NO_2 and N_2O_4 in the gas. Once the system attains equilibrium, the amount of each gas does not change, neither does the colour of the gas mixture. At the molecular level, however, both the forward and the reverse processes are still occurring.

Alternatively, this equilibrium system could be obtained by starting with only NO_2 gas. Initially the system would have a red-brown colour. As the reaction proceeds in the reverse direction, the colour will “fade” to yellow as N_2O_4 is produced.

Table 3.1.1 shows the results of three equilibrium experiments. Experiment 1 began with N_2O_4 only, Experiment 2 began with NO_2 only, and Experiment 3 began with a mixture of both gases. All three experiments were carried out at a constant temperature of 100 °C. Once the systems reached equilibrium, the final partial pressure of each gas was recorded. At the end of the three experiments, regardless of the initial composition of each species in the system, both N_2O_4 and NO_2 were present.

TABLE 3.1.1 THREE EQUILIBRIUM EXPERIMENTS WITH N_2O_4 AND NO_2

EXPERIMENT	SPECIES	P_{initial} (atm)	P_{final} (atm)
1	N_2O_4	1.000	0.226
	NO_2	0	1.548
2	N_2O_4	0	0.047
	NO_2	0.800	0.706
3	N_2O_4	1.000	0.431
	NO_2	1.000	2.138

What is the relationship between the equilibrium pressures? At first glance, it seems that all these experiments have one thing in common. In the equilibrium mixture, it appears that there is more NO_2 than N_2O_4 . However, it turns out that there is a consistent mathematical relationship between the equilibrium pressures of the reactants and products in all three of the above experiments. For this equilibrium this relationship is:

$$\frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \text{constant}$$

For any equilibrium, there is a mathematical relationship between the pressures or concentrations of the reactants and products. The symbol used for this relationship is K , which is known as the *equilibrium constant*. K sometimes includes a subscript that provides a bit more information about the equilibrium situation. For the previous example, the constant would be K_p . The subscript P indicates that the amounts of the species participating in the equilibrium were measured as pressures. If these amounts were measured in concentration units (e.g., mol L^{-1}), then the subscript would be C , as in K_C .

Effect of Temperature

Equilibrium constants are temperature dependent. If the temperature of the system changes, the numerical value of the equilibrium constant changes. Whether the value of K increases or decreases depends on whether the temperature is increased or decreased, and whether the reaction is endothermic or exothermic.

Homogeneous and Heterogeneous Equilibria

An equilibrium system may have all of its components in the same phase (physical state) or the components may be in different phases. If all the components are in the same phase, the system is a *homogeneous equilibrium*. If they are in different phases, the system is a *heterogeneous equilibrium*. The $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$ system shown in Table 3.1.1 is an example of a homogeneous equilibrium in the gas phase.

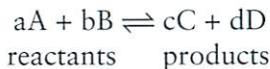
The equilibrium $\text{C(s)} + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$ is an example of a heterogeneous equilibrium because carbon is a solid while oxygen and carbon dioxide are gases. The equilibrium constant expression for this system would be:

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

Note that the solid is not included in the equilibrium constant expression. This is a general rule that will be explained further in the next section.

THE EQUILIBRIUM CONSTANT EXPRESSION

A general equilibrium reaction is written as:



and the general form of the equilibrium constant expression for this reaction, using concentrations, is:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (3.1.1)$$

In Equation 3.1.1 the $[\text{C}]$ and $[\text{D}]$ denote the products (numerator), and the $[\text{A}]$ and $[\text{B}]$ denote the reactants (denominator). The coefficients (a, b, c, d) in the balanced reaction have become the exponents in the concentrations. The K expression is unique to the chemical equation associated with it. The concentration of any solid, or of any solvent, is considered to be constant and is therefore omitted from the equilibrium constant expression.

Example 3.1.1. Writing Equilibrium Constant Expressions (In-Class Exercise)

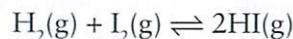
Write equilibrium constant expressions for the following reactions:

- a. $\text{H}_2\text{S(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)} + \text{S(s)}$
- b. $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$
- c. $\text{Ba}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \rightleftharpoons \text{BaSO}_4\text{(s)}$
- d. $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$

The next several examples show how the equilibrium constant expression is affected by the way the equilibrium reaction is written. In other words, how is K affected by reversing a reaction, multiplying or dividing a reaction, or the combination of multiple reactions?

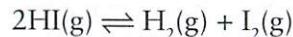
Reversing an Equilibrium Reaction

If the chemical equation for an equilibrium reaction is reversed, the expression for the equilibrium constant must be inverted. For example, in the equilibrium:



The equilibrium constant expression would be written as: $K = \frac{(\text{P}_{\text{HI}})^2}{\text{P}_{\text{H}_2} \text{P}_{\text{I}_2}}$

If the equilibrium is written in the reverse direction:

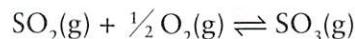


The equilibrium constant expression would be written as: $K' = \frac{\text{P}_{\text{H}_2} \text{P}_{\text{I}_2}}{(\text{P}_{\text{HI}})^2} = \frac{1}{K}$

Thus, when reversing an equilibrium reaction, the new K value is $1/K_{\text{original}}$.

Multiplying or Dividing an Equilibrium Reaction

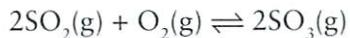
If the chemical equation for an equilibrium is multiplied by two, the K expression is squared. For example, in the equilibrium reaction:



the equilibrium constant expression is: $K = \frac{\text{P}_{\text{SO}_3}}{\text{P}_{\text{SO}_2} (\text{P}_{\text{O}_2})^{\frac{1}{2}}}$



If the reaction is multiplied by two, giving:



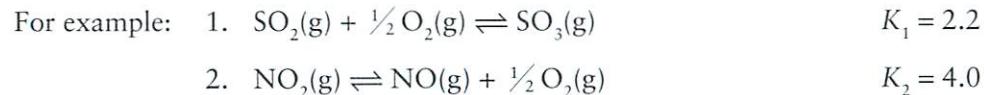
$$\text{then the equilibrium constant expression is: } K' = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 P_{\text{O}_2}} = K^2$$

Conversely, if the chemical equation is divided by two (multiplied by $\frac{1}{2}$), then the K expression is the square root of the original expression, $K' = K^{\frac{1}{2}}$.

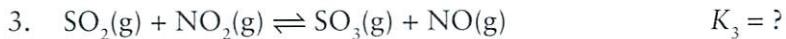
So, the general rule is that when an equilibrium reaction is multiplied by some coefficient, m , the new K value is K^m .

Combining Equilibria

If two or more equilibria are combined to produce an overall equilibrium, the equilibrium constant for the overall equilibrium can be determined.



These equilibria may be added together to give the overall equation:



To determine how to find K_3 , take a look at the expressions for K_1 , K_2 , and K_3 :

$$K_1 = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2}(P_{\text{O}_2})^{\frac{1}{2}}} \quad K_2 = \frac{P_{\text{NO}}(P_{\text{O}_2})^{\frac{1}{2}}}{P_{\text{NO}_2}} \quad K_3 = \frac{P_{\text{SO}_3} P_{\text{NO}}}{P_{\text{SO}_2} P_{\text{NO}_2}}$$

Multiplying $K_1 \times K_2$ will produce K_3 , and the numerical value is 8.8.

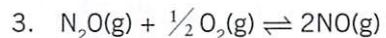
Thus, when adding reactions, multiply the K values: $K_{\text{new}} = K_1 \times K_2$.

Example 3.1.2. Determination of K Using Manipulation Rules (In-Class Exercise)

Given the following:



Determine the value of K_3 for:

**Significance of the Magnitude of K**

The numerical value of the equilibrium constant for a given reaction can range from very large to very small. The magnitude of the equilibrium constant is an indication of the relative amount of product or reactant present at equilibrium. If K is greater than 1, the equilibrium lies toward the right (product side) of the equation. This indicates that there are more products than reactants. If K is less than 1, the equilibrium lies toward the left (reactant side) of the equation. This indicates that there are more reactants than products.

Units for K , the Equilibrium Constant

Sometimes we write an equilibrium constant as K_p or K_c , where the subscript indicates whether the amounts of the species involved are expressed in atm or $M = \text{mol L}^{-1}$. But then we go on to say that equilibrium constants do not normally have units associated with them. How can this be?

The proper thermodynamic definition of the equilibrium constant is given in terms of properties called *activity* (for molecules in a solution) and *fugacity* (for gas-phase molecules). Both activity and fugacity are related to concentration and partial pressure, respectively, but carry no units (i.e., they are dimensionless).

For the examples we cover in this course, activity may be approximated as concentration in units of M; whereas fugacity may be approximated as partial pressure in units of atm (but not kPa). For this reason, only the units of M and atm should be used in calculations of K_c and K_p . The resulting equilibrium constants are to be treated as dimensionless quantities.



Determining *K* and Amounts

A numerical value for an equilibrium constant may be found if the equilibrium amounts of each species involved are known. Conversely, if the *K* is known, the stoichiometry of the reaction may allow the amounts of some species to be determined.

Example 3.1.3. Determining *K*

In the reaction:



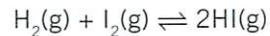
the equilibrium pressures are as follows: $P_{\text{PCl}_3} = 0.832 \text{ atm}$, $P_{\text{Cl}_2} = 0.712 \text{ atm}$, and $P_{\text{PCl}_5} = 0.276 \text{ atm}$. Determine *K* for the reaction.

Solution:

$$K = \frac{P_{\text{Cl}_2} \times P_{\text{PCl}_3}}{P_{\text{PCl}_5}} = \frac{(0.832)(0.712)}{(0.276)} = 2.15$$

Example 3.1.4. Determining Equilibrium Amounts and *K* (In-Class Exercise)

Consider the reaction:



Suppose the reaction begins with only 1.00 atm each of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$. At equilibrium, the system was found to contain 0.2125 atm each of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$. Determine the equilibrium pressure of $\text{HI}(\text{g})$ and a value of the equilibrium constant.

THE REACTION QUOTIENT, *Q*

A system can be studied at any time during the course of a reaction, not just initially or at equilibrium. If the amounts of products and reactants can be determined, a quantity known as the *reaction quotient* may be calculated. This number indicates whether the system is at equilibrium, *and* the direction in which the reaction must proceed to attain equilibrium.

For the general reaction: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

Using concentrations, the expression for the reaction quotient, Q , is:

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

The expression for the reaction quotient in terms of pressures would be similar:

$$Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

The reaction quotient expression is the same as the equilibrium constant expression except that the concentrations (or pressures) used to calculate Q are not necessarily the equilibrium concentrations (or pressures). Comparing the numerical value of Q to that of K will indicate if the reaction is at equilibrium and, if not, whether more products or more reactants must be made to attain equilibrium.

Consider the equilibrium for the production of ammonia:



At some point in the reaction, the following measurements are made:

$$P_{\text{NH}_3} = 0.913 \text{ atm}, P_{\text{N}_2} = 0.131 \text{ atm}, P_{\text{H}_2} = 0.0518 \text{ atm}$$

Is this system at equilibrium? If not, in which direction must the reaction proceed to attain equilibrium? The reaction quotient expression for the reaction is:

$$Q = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.913)^2}{(0.131)(0.0518)^3} = 4.57 \times 10^4$$

A system is at equilibrium only when $Q = K$. The value of Q is less than the value of K in this case, so the system is not at equilibrium. The smaller Q value means the system either does not have enough product(s) or has too much reactant, and the reaction must proceed in a forward (\rightarrow) direction to attain equilibrium.

If the numerical value of Q is greater than K , the system must proceed in the reverse (\leftarrow) direction to attain equilibrium, because there is either too much product or not enough reactant.



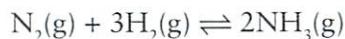
LE CHÂTELIER'S PRINCIPLE

Once a system has reached equilibrium, the concentrations or pressures of the reactants and products remain constant. This does not mean that the system has stopped reacting, only that the forward and reverse rates are equal. Changing the temperature or the pressure, or adding or removing one of the chemical species, will disturb the equilibrium. The system will react in one direction or the other to re-establish equilibrium. After this occurs, the concentrations or pressures at equilibrium will be different than they were before the system was disturbed. The phrase used is “the position of the equilibrium will change.” The value of the equilibrium constant does not change unless the temperature changes.

The manner in which these changes are accomplished was summed up in a famous principle originated by French chemist Henri Le Châtelier in 1884:

If a chemical system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of a participant in the equilibrium, the equilibrium will shift in such a way as to minimize the disturbance.

Some of the applications of this principle may be illustrated using the equilibrium:



The numerical value of the equilibrium constant will not change, unless the temperature changes, so at 298.15 K, $K_p = 3.6 \times 10^8$.

Concentration Changes

Suppose that the concentration of H_2 is increased in the reaction above. The system will attempt to use some of this additional H_2 . The reaction will proceed to the right, also using some of the N_2 , resulting in an increase in the concentration of NH_3 . The overall effect is that the concentration of $\text{H}_2(\text{g})$ will be larger, the concentration of $\text{N}_2(\text{g})$ will be smaller, and the concentration of $\text{NH}_3(\text{g})$ will be larger.

Now suppose that some of the $\text{NH}_3(\text{g})$ is removed by condensing it into $\text{NH}_3(\text{l})$. The system will attempt to make more NH_3 . Once again, the reaction will proceed in the forward direction, decreasing the amounts of N_2 and H_2 .

If NH_3 is added, the opposite effect is seen and the reaction will proceed in the reverse direction toward the reactants. The amounts of both N_2 and H_2 will increase. These changes can be observed mathematically using the equilibrium constant expression, and comparing K with Q . At equilibrium:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

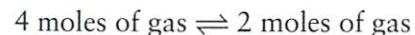
If the concentration of H_2 is increased, Q will be smaller than K . Therefore, the reaction will proceed in the forward direction until $Q = K$ again. If the concentration of NH_3 is increased, Q will be larger than K . The reaction must proceed in the reverse direction until $Q = K$.

Pressure Changes

Another way of disturbing a gaseous equilibrium system is to change the total pressure of the system. If the equilibrium pressure of a reactant or product is changed, the result is the same as a change in concentration. (The pressure of a particular species is directly proportional to the number of moles of that species.)

The pressure of a system involving gases may be disturbed by changing the volume of the system. Increasing the volume of a system results in a drop in pressure of each gas. If the volume of a system is increased the reaction will proceed in the direction that produces more moles of gas, if that is possible. This will increase the pressure. If the volume of a system is decreased, pressures will increase and the reaction will proceed in the direction that will produce fewer moles of gas.

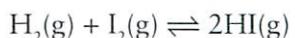
For example, if there are four moles of gas on the reactant side and two moles of gas on the product side of an equilibrium reaction, an increase in the volume of the container would result in the reaction proceeding in the reverse direction. Decreasing the volume of the container would result in the reaction proceeding in the forward direction.



Thus, the reaction will proceed in a direction that produces more gas or less gas, depending on whether the volume is increased or decreased. If an inert gas is added to the gaseous equilibrium system, the result will be an increase in the total pressure, but there will not be any changes to the partial pressures of the reactant and product gases. Therefore, there will be no change in the position of the equilibrium.



Systems involving just solids and liquids are not affected by changing the volume of a container. Systems that involve both gases and solids or liquids will be affected. If the number of moles of reactant gases and product gases are the same, as in:



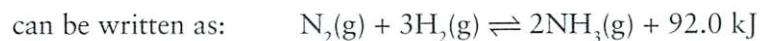
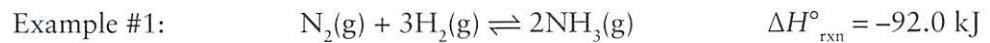
then changing the volume will not effect the position of the equilibrium.

All of the above changes have been accomplished by changing some condition of the equilibrium system at a constant temperature, which means that the numerical value of K has not changed.

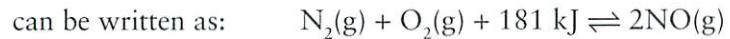
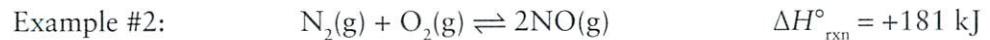
Relationship Between Temperature and K Values

If the temperature of the system is changed, the value of the equilibrium constant will change. The explanation for this involves looking at the change in enthalpy (ΔH) that accompanies a reaction. If ΔH for a reaction is positive, the reaction is endothermic and heat is absorbed from the surroundings. If ΔH for a reaction is negative, the reaction is exothermic and heat is released to the surroundings.

To understand how temperature changes affect the position of the equilibrium, one has to include the enthalpy change as a reactant or product in the equation.



This reaction produces heat and the temperature of the surroundings will rise.



This reaction requires or absorbs heat, resulting in a drop in the temperature of the surroundings. For each of these reactions, one could either increase or decrease the system temperature.

In an exothermic reaction, increasing the temperature has the same effect as increasing the amount of one of the products. Le Châtelier's principle indicates that this will result in a shift of the equilibrium to the left, increasing the amounts of the reactants and decreasing the value of K . The reverse is true if the temperature is lowered. This would be similar to removing one of the products. The equilibrium

will shift to the right, increasing the amounts of the products and increasing the value of K .

Adding heat in an endothermic reaction has the same effect as increasing the amount of one of the reactants. Therefore, increasing the temperature leads to an increase in the amounts of the products. The equilibrium will shift to the right, resulting in an increase in K . Removing heat is similar to decreasing the amount of one of the reactants. To offset this disturbance, the equilibrium will shift to the left, increasing the amounts of the reactants and decreasing K .

GIBBS FREE ENERGY AND THE EQUILIBRIUM CONSTANT

Recall that the Gibbs free energy change (ΔG) can be used to determine whether a reaction proceeds spontaneously at constant temperature and pressure. In summary, when:

- $\Delta G < 0$ The reaction will proceed spontaneously as written.
- $\Delta G = 0$ The system is at equilibrium. The number of moles of reactant and product will not change over time.
- $\Delta G > 0$ The reaction will not occur spontaneously as written; instead, the reverse process will occur spontaneously.

ΔG° is the free energy change under standard conditions. This means that the temperature is 298.15 K (25 °C), all gases are at pressure of 1 atm and all species in solution have a concentration of 1 M. A positive value for ΔG° indicates that a process is nonspontaneous *under standard conditions*. This does not mean that a reaction does not proceed at all, only that it proceeds to a very small extent.

ΔG° is also related to equilibrium. If ΔG° is positive, the equilibrium lies to the left (reactant side) and K is small. Conversely, if ΔG° is negative, the equilibrium lies to the right (product side) and K is large.

A familiar example of equilibrium is the vapourization of water:



Even though the ΔG° is positive, some water does evaporate but the $\text{H}_2\text{O(g)}$ produced has a vapour pressure less than 1 atm. At 25 °C the equilibrium lies far to the left, in favour of the reactants.



What is the relationship between ΔG° and K ? First, the relationship between ΔG and ΔG° (i.e., free energy under nonstandard and standard conditions) is:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3.1.2)$$

where Q is the reaction quotient. Because $\Delta G = 0$ and $Q = K$ at equilibrium, Equation 3.1.2 can be rearranged to show the relationship between ΔG° and K :

$$\Delta G^\circ = -RT \ln K \quad (3.1.3)$$

In Equation 3.1.3:

- ΔG° is the standard Gibbs free energy for the reaction in joules per mole
- R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- $T = 298.15 \text{ K}$ (since ΔG° values are at 298.15 K)
- K is the equilibrium constant (K_p for gas-phase reactions, K_c for reactions in solution)

Note that for Equation 3.1.3 to be used correctly, ΔG° must be in joules per mole (J mol^{-1}) because R , the gas constant, is in units of $\text{J mol}^{-1} \text{ K}^{-1}$. (Do not confuse the K for Kelvin with the italicized K used for the equilibrium constant.)

Example 3.1.5. Determining K from ΔG° (In-Class Exercise)

Determine the equilibrium constant for the vapourization of water.

The standard free energy change for a reaction is also related to enthalpy and entropy changes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.1.4)$$

By substituting for ΔG° from Equation 3.1.3, the following relationship emerges:

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\text{Dividing both sides by } -RT: \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3.1.5)$$

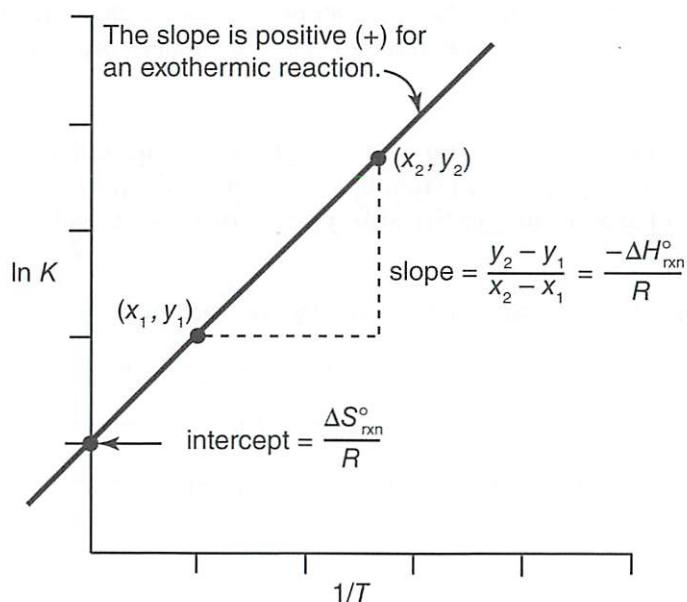
While ΔG° varies with temperature as shown in Equation 3.1.4, both ΔH° and ΔS° vary little over the temperature range of most reactions. Equation 3.1.5 can therefore be used to find K values at temperatures other than 298.15 K .

Equation 3.1.5 can be rearranged to correspond with the general equation for a straight line, $y = mx + b$ (m = slope; b = intercept point on y -axis):

$$\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (3.1.6)$$

$$y = m x + b$$

Thus, a plot $\ln K$ versus $1/T$ gives a straight line with a slope of $-\Delta H_{\text{rxn}}^\circ/R$ and a y -intercept of $\Delta S_{\text{rxn}}^\circ/R$.



Example 3.1.6. Determining $\Delta H_{\text{rxn}}^\circ$ from K and T (In-Class Exercise)

For a given reaction, a series of K values were determined at various temperatures. If the values of K were 6.0 and 330 at 1333 K and 800 K respectively, what is the value of $\Delta H_{\text{rxn}}^\circ$?



THE VAN'T HOFF EQUATION

In the late 19th century, Dutch chemist Jacobus Henricus van't Hoff used a derivative of Equation 3.1.6 to determine K values at different temperatures.

Writing Equation 3.1.6 for two sets of points, $(\ln K_1, 1/T_1)$ and $(\ln K_2, 1/T_2)$:

$$\ln K_1 = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R} \quad \text{and} \quad \ln K_2 = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R}$$

Then subtracting $\ln K_2 - \ln K_1$:

$$\begin{aligned}\ln K_2 - \ln K_1 &= \left[\frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R} \right] - \left[\frac{-\Delta H^\circ}{R} \left(\frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R} \right] \\ &= \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} \right) + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} \right)\end{aligned}$$

Thus,

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3.1.7)$$

Equation 3.1.7, known as the van't Hoff equation, can be used to determine K at a second temperature, T_2 , given $\Delta H^\circ_{\text{rxn}}$, K_1 and T_1 . If K is known at two different temperatures, the equation may also be used to calculate $\Delta H^\circ_{\text{rxn}}$. Another practical use for the van't Hoff equation is to determine the appropriate temperature at which to carry out a reaction.

For example, in the reaction:



$K_C = 4.61 \times 10^{-3}$ at 25°C , and $\Delta H^\circ_{\text{rxn}} = +57.2 \text{ kJ}$. From the magnitude of K_C , the equilibrium lies to the left at this temperature; there is much, much more N_2O_4 than there is NO_2 . If the desired species is NO_2 , the equilibrium must be shifted to the right in favour of the product. To accomplish this, the numerical value of K must be increased to reflect the greater amount of product.

Since $\Delta H^\circ_{\text{rxn}}$ is positive, this is an endothermic reaction so an increase in temperature will cause the equilibrium to shift in the forward direction. How much of a temperature increase will be necessary? Suppose one wants a K value of 2.00, which would clearly result in more product. The temperature necessary to achieve this value of K , using the van't Hoff equation, is found by:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ_{\text{rxn}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$
$$\ln \frac{2.00}{4.61 \times 10^{-3}} = \frac{57,200 \text{ J}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2} \right)$$

Note that the value of $\Delta H^\circ_{\text{rxn}}$ was converted to joules to match the units of R , the gas constant, and the temperature was converted to Kelvin, also to match the units of the gas constant. Solving, $T_2 = 404 \text{ K}$ or 131°C .

Example 3.1.7. Predicting K at Different T (In-Class Exercise)

A reaction has $\Delta H^\circ = -41.2 \text{ kJ mol}^{-1}$. If $K = 201$ at 250 K , what is K at 725 K ?



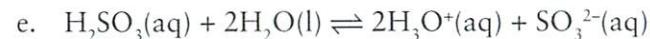
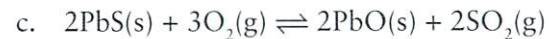
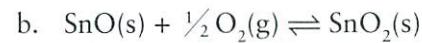
Section 3.1 Review Problems

1. Write the equilibrium constant expressions for the following equilibria:
 - a. $2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 4\text{H}_2(\text{g})$
 - b. $\text{Na}_2\text{O}_2(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$
 - c. $\text{I}_2(\text{s}) + 3\text{XeF}_2(\text{s}) \rightleftharpoons 2\text{IF}_3(\text{s}) + 3\text{Xe}(\text{g})$
2. Write the chemical equations for the equilibrium systems that would lead to the following equilibrium constant expressions:

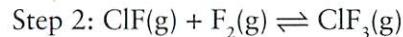
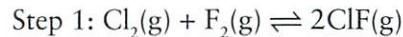
a. $K = \frac{(P_{\text{H}_2\text{O}})^2 (P_{\text{Cl}_2})^2}{(P_{\text{HCl}})^4 P_{\text{O}_2}}$

b. $K = \frac{(P_{\text{H}_2\text{O}_2})^2}{(P_{\text{H}_2\text{O}})^2 P_{\text{O}_2}}$

3. Write the equilibrium constant expression for each of the following reactions. Classify each as homogeneous or heterogeneous. For gaseous equilibria, use partial pressures.



4. The two-step fluorination of chlorine gas produces ClF_3 as the only product.



What is the correct equilibrium constant expression for the overall reaction?

a. $K = \frac{(P_{\text{ClF}})^2}{P_{\text{Cl}_2} P_{\text{F}_2}}$

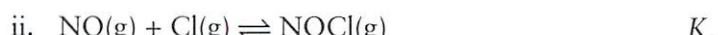
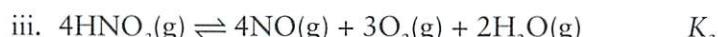
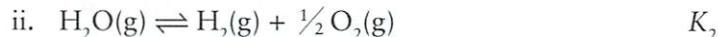
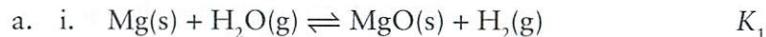
d. $K = \frac{P_{\text{ClF}_3}}{P_{\text{Cl}_2} P_{\text{F}_2}}$

b. $K = \frac{P_{\text{ClF}_3}}{P_{\text{ClF}} P_{\text{F}_2}}$

e. $K = \frac{P_{\text{ClF}_3}}{(P_{\text{ClF}})^2 P_{\text{F}_2}}$

c. $K = \frac{(P_{\text{ClF}_3})^2}{P_{\text{Cl}_2} (P_{\text{F}_2})^3}$

5. In each of the following examples, three related chemical reactions are shown, with equilibrium constants K_1 , K_2 , and K_3 . In each case, express K_3 as a function of K_1 and K_2 .



6. Given: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$; $K_p = 49$ at 730 K,

Determine K_p for: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ at 730 K.



7. Given: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$; $K_p = 0.77$ at 1020 K,
Determine K_p for: $3\text{H}_2\text{O}(\text{g}) + 3\text{CO}(\text{g}) \rightleftharpoons 3\text{H}_2(\text{g}) + 3\text{CO}_2(\text{g})$ at 1020 K.
8. Methanol, CH_3OH , can be produced from the reaction of hydrogen gas, H_2 , and carbon monoxide gas, CO, if a suitable catalyst is used. This process is a chemical equilibrium.
- Write a balanced equation for this equilibrium.
 - Write the equilibrium constant expression for this equilibrium.
 - At 227 °C, the equilibrium partial pressures of CO, H_2 , and CH_3OH are as follows: 0.711 atm, 0.177 atm, and 0.00136 atm. Determine K_p for this reaction.
 - What would the equilibrium constant be at 227 °C for the decomposition reaction of 2.0 moles of CH_3OH to CO and H_2 ?
9. Use the van't Hoff equation to determine the $\Delta H_{\text{rxn}}^\circ$ for the following equilibrium reaction given the K and T values at right:



10. Given: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$; $K_c = 0.77$ at 1020 K,

Determine K_p at 850 K using the data below.

$$\Delta H_f^\circ (\text{kJ mol}^{-1}): \text{CO}_2(\text{g}) = -393.5 \text{ kJ}; \text{H}_2\text{O}(\text{g}) = -241.8; \text{CO}(\text{g}) = -110.5$$

11. In an equilibrium reaction, the following values of $\ln K$ versus $1/T$ were recorded and plotted to give a straight line:

$\frac{1}{T}$	$\ln K$
$8.0 \times 10^{-4} \text{ K}^{-1}$	-2.0
$9.0 \times 10^{-4} \text{ K}^{-1}$	0
$10.0 \times 10^{-4} \text{ K}^{-1}$	2.0
$11.0 \times 10^{-4} \text{ K}^{-1}$	4.0

Given these data, what was the $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$?

12. Determine the $\Delta H^\circ_{\text{rxn}}$ in kJ for an equilibrium reaction which has $K_1 = 2.5 \times 10^2$ at 25 °C and $K_2 = 6.5$ at 95 °C.
13. An equilibrium reaction has $K_1 = 6.5 \times 10^{-2}$ at 85 °C and $\Delta H^\circ_{\text{rxn}} = -46.5 \text{ kJ mol}^{-1}$. What is K at 235 °C?
14. An equilibrium reaction has $K_1 = 4.5 \times 10^{-2}$ at 110 °C and $\Delta H^\circ_{\text{rxn}} = -65.2 \text{ kJ mol}^{-1}$. At what temperature, in K, is $K = 6.50$?

3.2 Solubility of Ionic Compounds

OBJECTIVES

After studying this topic, you should be able to:

- Use K_{sp} to find the solubility of a compound in water or in an aqueous solution containing a common ion.
- Given a K_{sp} value, determine the pH of a solution and how the solubility of a substance changes with pH.
- Given K_{sp} values, identify and determine the concentrations of the ions that will remain in solution when two different solutions are mixed.

WHY IS SOLUBILITY IMPORTANT?

It would be difficult to overestimate the importance of solution processes and precipitation reactions as there are numerous examples encountered in our daily lives. Processes involving the solubility of ionic compounds are important in many areas of scientific endeavour, from biology, biochemistry, and medicine, to earth sciences, as well as in industrial chemistry.

Calcium, for example, is an extremely important mineral both in and out of solution in our bodies. In our bloodstream, its ionic form (Ca^{2+}) participates in nerve transmission, muscle contraction, blood clotting, blood pressure regulation, and hormone secretion. The main component in bones and teeth is a highly insoluble calcium complex known as hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The solubility of this complex may be affected by large amounts of acid which, in the case of tooth enamel, will lead to tooth decay.

There is a delicate balance between the calcium that exists as a solid ionic compound in bones and teeth, and the calcium in our bloodstream. If blood levels of this element are too low, processes come into play that release calcium from bones and allow it to dissolve into the ionic form. If an excess of phosphate ion is also present, calcium phosphate may form and produce kidney stones.

In this topic, the solubility of relatively insoluble ionic compounds is examined.

A BRIEF REVIEW OF SOLUBILITY AND PRECIPITATION

The *solubility* of a substance is the amount of that substance that will dissolve in a certain volume of a specific solvent, and is usually expressed in grams per litre or in moles per litre. The degree of solubility is roughly defined as:

- Soluble compound: 10 g or more can dissolve in a litre of solvent.
- Slightly soluble compound: 0.1 to 10 g can dissolve in a litre of solvent.
- Insoluble compound: less than 0.1 g can dissolve in a litre of solvent.

The figures above apply at room temperature. In general, ionic compounds become more soluble as the temperature increases.

Table 3.2.1 provides guidelines that can be used to predict if an ionic compound (salt) will be soluble or insoluble.

TABLE 3.2.1 SOLUBILITY GUIDELINES FOR IONIC SOLIDS

PRIORITY	GUIDELINES <i>Salts of...</i>		EXCEPTIONS	
1st	Group 1 cations, NH_4^+	<i>are soluble</i>	LiF , Li_2CO_3	<i>are insoluble</i>
2nd	NO_3^- , CH_3COO^- , HCO_3^- , ClO_4^-	<i>are soluble</i>		
3rd	Ag^+ , Pb_2^+ , Hg_2^{2+}	<i>are insoluble</i>	AgF	<i>is soluble</i>
4th	F^- , Cl^- , Br^- , I^-	<i>are soluble</i>	Group 2 fluorides	<i>are insoluble</i>
5th	CO_3^{2-} , PO_4^{3-} , CrO_4^{2-} , S^{2-} , O^{2-} , OH^-	<i>are insoluble</i>	Group 2 sulfides Ca^{2+} , Sr^{2+} , and Ba^{2+} hydroxides	<i>are soluble</i>
6th	SO_4^{2-}	<i>are soluble</i>	Ca^{2+} , Sr^{2+} , and Ba^{2+} sulfates	<i>are insoluble</i>

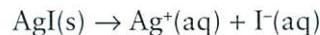


Salts of ions in the top left section of Table 3.2.1 are all *soluble* unless they are salts of one of the ions listed as an exception. Conversely, salts of ions in the bottom left section are all *insoluble* unless they are salts of one of the ions listed as an exception.

THE SOLUBILITY PRODUCT

A *solvent* is a liquid or a gas that dissolves another solid, liquid, or gas. The substances that dissolve in a solvent are called the *solutes* of the resultant solution. *Solubility* is defined as the amount of a given substance that dissolves in a given volume of solvent at a given temperature, and may be expressed in g L⁻¹ or mol L⁻¹.

When an ionic solid dissolves in water, it dissociates into hydrated (solvated) ions. For example, suppose one slowly added small amounts of an ionic solid such as silver iodide, AgI(s), to a beaker of pure water. The following reaction would start to occur:



As the dissolution proceeds, the concentration of ions would increase little by little as more and more of the silver iodide was added. Eventually, no more additional silver iodide would dissolve in the solution.

At this point an equilibrium is established between the undissolved solid and the free ions, and the solution is said to be *saturated*. An equilibrium expression can be written for this process:



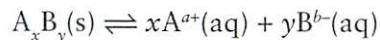
and an equilibrium constant can be defined as:

$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

where [Ag⁺] and [I⁻] are the concentrations of the ions in mol L⁻¹ and K_{sp} is an equilibrium constant called the *solubility product* or the *solubility product constant*.

Salts that are very soluble have a very large K_{sp} value. These dissolutions essentially go to completion and are denoted by a one-way arrow (→). For compounds with low solubility, an equilibrium may be established and the familiar equilibrium arrow (↔) is used.

In general, for the dissolution of an ionic solid of composition A_xB_y , the equilibrium reaction is written as:



and the K_{sp} expression for this heterogeneous equilibrium is written as:

$$K_{sp} = [A^{a+}]^x[B^{b-}]^y$$

Note that the pure solid is not included in the equilibrium expression. This is because excess solid does not affect the position of the equilibrium. More solid provides more surface area from which dissolution can occur, but reformation of solid also occurs at the surface. Doubling the surface area doubles the rate of dissolution but also the rate of precipitation, thus there is no effect on the equilibrium position.

Example 3.2.1. Writing K_{sp} Expressions (In-Class Exercise)

Write the K_{sp} expressions for CaCO_3 , Mg(OH)_2 , and $\text{Sr}_3(\text{PO}_4)_2$

It is also important to distinguish between the concepts of *solubility* and the *solubility product constant*. The solubility product constant is an equilibrium constant and is thus always the same for a given solid at a given temperature. K_{sp} values vary only with temperature, and the ones shown in Table 3.2.2 are at 25 °C. On the other hand, at a given temperature the amount of solid that will dissolve will vary depending on other conditions such as the presence of ions in solution, thus giving an infinite number of possible values.

Saturated and Unsaturated Solutions

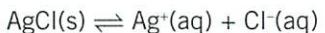
The term *saturated* implies that there is an equilibrium between the solid and the ions in solution. If the quantity of a species in solution is less than that required for equilibrium with the solid, the solution is said to be *unsaturated*. If more solid is added to an unsaturated solution, it dissolves until the solution is saturated (at which point there is solid in equilibrium with solvated ions).



Example 3.2.2. Solubility of AgCl

Find the solubility of AgCl ($K_{sp} = 1.7 \times 10^{-10}$) in water.

Solution: The equation for dissolution of AgCl is:



Initial:	solid	0	0
$\Delta:$	$-x$	$+x$	$+x$
Equil:	solid - x	x	x

where x is the amount of AgCl that dissolves (mol L⁻¹). x also equals [Ag⁺] and [Cl⁻] at equilibrium.

$$\begin{aligned}K_{sp} &= 1.7 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] \\&= (x)(x)\end{aligned}$$

Therefore: $x = \sqrt{1.7 \times 10^{-10}} = 1.3 \times 10^{-5} M$ = solubility of AgCl.

TABLE 3.2.2 K_{sp} VALUES FOR SELECTED COMPOUNDS AT 25 °C

CATEGORY	FORMULA	K_{sp}	CATEGORY	FORMULA	K_{sp}
Bromides	PbBr ₂	4.6×10^{-5}	Hydroxides (cont'd)	Fe(OH) ₂	1.8×10^{-15}
	Hg ₂ Br ₂	1.3×10^{-22}		Fe(OH) ₃	1.0×10^{-38}
	AgBr	5.0×10^{-13}		Pb(OH) ₂	4.2×10^{-15}
Carbonates	BaCO ₃	1.6×10^{-9}		Mg(OH) ₂	8.9×10^{-12}
	CaCO ₃	4.7×10^{-9}	Iodides	PbI ₂	8.3×10^{-9}
	CuCO ₃	2.5×10^{-10}		Hg ₂ I ₂	4.5×10^{-29}
	FeCO ₃	2.1×10^{-11}		Agl	8.5×10^{-17}
	MgCO ₃	1.0×10^{-15}	Phosphates	Ba ₃ (PO ₄) ₂	6.0×10^{-39}
	Ag ₂ CO ₃	8.2×10^{-12}		Ca ₃ (PO ₄) ₂	1.3×10^{-32}
Chlorides	PbCl ₂	1.7×10^{-5}		Ag ₃ PO ₄	1.8×10^{-18}
	Hg ₂ Cl ₂	1.1×10^{-18}		Sr ₃ (PO ₄) ₂	1.0×10^{-31}
	AgCl	1.7×10^{-10}	Sulfates	BaSO ₄	1.5×10^{-9}
Fluorides	BaF ₂	2.4×10^{-5}		CaSO ₄	2.4×10^{-5}
	CaF ₂	3.4×10^{-11}		PbSO ₄	1.3×10^{-8}
	PbF ₂	4.0×10^{-8}		Ag ₂ SO ₄	1.2×10^{-5}
	MgF ₂	8.0×10^{-8}		SrSO ₄	7.6×10^{-7}
	SrF ₂	7.9×10^{-10}	Sulfides	CuS	8.0×10^{-37}
Hydroxides	Al(OH) ₃	5.0×10^{-33}		FeS	6.3×10^{-18}
	Ba(OH) ₂	5.0×10^{-3}		PbS	7.0×10^{-29}
	Ca(OH) ₂	1.4×10^{-6}		HgS	1.6×10^{-54}
	Cu(OH) ₂	1.6×10^{-19}		Ag ₂ S	5.5×10^{-51}

Example 3.2.3. Solubility of PbCl_2 (In-Class Exercise)

Find the solubility of PbCl_2 ($K_{\text{sp}} = 1.7 \times 10^{-5}$) in water at 25 °C.

Example 3.2.4. Solubility of $\text{Sr}_3(\text{PO}_4)_2$ (In-Class Exercise)

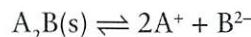
Find the solubility of $\text{Sr}_3(\text{PO}_4)_2$ in water at 25 °C given its $K_{\text{sp}} = 1.0 \times 10^{-31}$. How many litres of water are required to dissolve 0.25 mol of $\text{Sr}_3(\text{PO}_4)_2$?

Example 3.2.5. Solubility and K_{sp} of PbI_2 (In-Class Exercise)

The solubility of lead iodide (PbI_2) in water at 25 °C is 0.588 g L⁻¹. What is the K_{sp} of PbI_2 ?

The Reaction Quotient, Q

Suppose one dissolves the compound A_2B to produce a saturated solution:



The K_{sp} expression may be used for the system at equilibrium. The reaction quotient, Q , also known as the *ion product*, would be written:

$$Q = [A^+]^2 [B^{2-}]$$

For a saturated solution, $Q = K_{sp}$ (the system is at equilibrium). As discussed in the previous topic, the reaction quotient expression is the same as the equilibrium constant expression except that the concentrations used to determine Q are not necessarily the equilibrium concentrations. At given concentrations of ions in solution, the K_{sp} value and the Q value can be compared to determine whether a solid (precipitate) will be present:

1. When $Q < K_{sp}$, no solid will be present. All ions will remain in solution.
2. When $Q = K_{sp}$, the system is in equilibrium (saturated).
3. When $Q > K_{sp}$, a solid will be formed from the ions in solution. This is a precipitation reaction and the solution is said to be *supersaturated* (i.e., the solution has an ion concentration greater than the equilibrium values).

The reaction quotient is especially useful when the ions that react to form a salt come from two different sources.

Example 3.2.6. Precipitation of $PbCl_2$ (In-Class Exercise)

If 100 mL of 0.030 M $Pb(NO_3)_2$ and 150 mL of 0.040 M KCl are mixed, does precipitation of $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) occur?



Example 3.2.7. Precipitation of PbSO_4 (In-Class Exercise)

How much solid $\text{Pb}(\text{NO}_3)_2$ must be added to 10.0 L of 0.0010 M Na_2SO_4 for a precipitate of PbSO_4 ($K_{\text{sp}} = 1.3 \times 10^{-8}$) to form? Assume no change in volume when the solid is added.

Example 3.2.8. Determination of K_{sp} (In-Class Exercise)

When 133 mL of 0.0500 M KF is added to 200 mL of 0.0100 M $\text{Ba}(\text{NO}_3)_2$, the first trace of BaF_2 precipitate is seen. What is the K_{sp} for BaF_2 ?

THE COMMON ION EFFECT

Thus far the solubility of ionic solids in pure water has been discussed. Often the situation is more complex and the solution may already contain an ion in common with the dissolving salt. This *common ion effect* can significantly reduce the solubility of the solid relative to that in pure water.

In a previous example, the solubility of AgCl in pure water at 25 °C was found to be $1.3 \times 10^{-5} M$. How does one determine the solubility of AgCl in a solution where the $[NaCl] = 0.20 M$? (NaCl is completely soluble; therefore, $[Cl^-] = 0.20 M$.)

Let x be the number of moles of AgCl that must dissolve per litre (the solubility) to establish equilibrium. The equation for the dissolution of AgCl is:



Initial:	solid	0	0.20
Δ:	$-x$	$+x$	$+x$
Equil:	solid $-x$	x	$0.20 + x$

Now, at equilibrium:

$$K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$$

$$x(0.20 + x) = 1.7 \times 10^{-10}$$

This equation yields the quadratic $x^2 + 0.20x = 1.7 \times 10^{-10}$. This may be solved as is, or an approximation (simpler method) may be used. According to Le Châtelier's principle, adding Cl^- to the equilibrium will cause the reaction to shift to the left, toward the reactant (AgCl) side. Thus, very little extra Cl^- will be produced as a result of dissolution of AgCl and the value for x will be smaller than in pure water. In addition, AgCl is already only sparingly soluble ($K_{sp} = 1.7 \times 10^{-10}$).

In this case it is reasonable to assume that $x \ll 0.20$ or that:

$$0.20 + x \approx 0.20, \text{ therefore:}$$

$$x(0.2) = 1.7 \times 10^{-10}$$

$$x = 8.5 \times 10^{-11} M = \text{solubility of AgCl in } 0.20 M NaCl.$$



The solubility of AgCl has been very substantially reduced over that in pure water (from $1.3 \times 10^{-5} M$ to $8.5 \times 10^{-10} M$). This reduction in solubility is the result of the common ion effect.

Example 3.2.9. Solubility of PbCl₂ in Aqueous KCl (In-Class Exercise)

Find the solubility of PbCl₂ ($K_{sp} = 1.7 \times 10^{-5}$) in 0.20 M KCl. Compare your answer to that obtained in the "Solubility of PbCl₂" In-Class Exercise example on page 3-29.

Example 3.2.10. Precipitation of SrCrO₄ (In-Class Exercise)

Find the concentrations of Sr²⁺ and CrO₄²⁻ remaining in solution after mixing 50.0 mL of 0.30 M Sr(NO₃)₂ with 100 mL of 0.40 M K₂CrO₄.

$$K_{sp} \text{ for SrCrO}_4 = 3.6 \times 10^{-5}$$

Section 3.2 Review Problems

1. If the solubilities of AgBr and SrF₂ are 1.3×10^{-4} g L⁻¹ and 0.13 g L⁻¹ respectively, determine their K_{sp} values.
2. What are the solubilities in mol L⁻¹ of MgCO₃ ($K_{sp} = 1.0 \times 10^{-15}$) and Mn(OH)₂ ($K_{sp} = 2.0 \times 10^{-13}$)? What is the pH of a saturated solution of Mn(OH)₂?
3. The solubility of strontium fluoride (SrF₂) in water is 0.109 g L⁻¹. What is the K_{sp} of SrF₂?
4. For an ionic compound in solution, define the terms *ion product* (or *reaction quotient*, Q) and *solubility product*, K_{sp} . Under what circumstances does Q equal the solubility product?
5. The pH of a saturated solution of Cd(OH)₂ in pure water is 9.56.
 - a. How many grams of Cd(OH)₂ are dissolved in 1 L of this solution?
 - b. What volume of pure water would be needed to dissolve 1.0 g of Cd(OH)₂?
 - c. What is the K_{sp} for Cd(OH)₂?
6. Which of the following statements is/are correct?
 - a. If solid AB is in equilibrium with an aqueous solution already containing [A⁺] and [B⁻] ions, [A⁺] and [B⁻] must always be equal.
 - b. PbCl₂ is less soluble in KCl solution than in pure water because the presence of Cl⁻ reduces the K_{sp} value of PbCl₂.
 - c. A slightly soluble metal hydroxide, M(OH)₂, will dissolve more readily as the pH of the solution is increased.
7. Manganese sulfide (MnS) has $K_{sp} = 5 \times 10^{-14}$. What mass of solid manganese chloride (MnCl₂) would have to be added to 100 mL of a 0.025 M Na₂S solution to cause precipitation of MnS to begin?
8. A 0.0010 M solution of barium nitrate, Ba(NO₃)₂, is added gradually to 200 mL of 0.040 M NaF. Precipitation of BaF₂ begins after 35 mL of the Ba(NO₃)₂ solution have been added. What is the K_{sp} for BaF₂?

9. When solid barium fluoride, BaF_2 , equilibrates with pure water at 25°C , the fluoride concentration is 0.015 M . Determine K_{sp} for BaF_2 . What volume of water would be required to dissolve 1.00 g of BaF_2 ?
10. Lead hydroxide, $\text{Pb}(\text{OH})_2$, has $K_{\text{sp}} = 4.2 \times 10^{-15}$. What is the $[\text{Pb}^{2+}]$ in a saturated solution of $\text{Pb}(\text{OH})_2$ at a fixed pH of 5.30 ?
11. Joe Student is trying to make a very dilute AgNO_3 solution by diluting 1.0 mL of 0.010 M AgNO_3 to 1.0 L . Carelessly, Joe uses tap water instead of distilled water for the dilution. If the tap water has a chloride ion concentration of $2.0 \times 10^{-4}\text{ M}$, will AgCl precipitate? (K_{sp} for $\text{AgCl} = 1.7 \times 10^{-10}$)
12. $1 \times 10^{-4}\text{ M}$ potassium chromate (K_2CrO_4) is added drop-by-drop to 200 mL of 0.0020 M AgNO_3 solution. Precipitation of silver chromate (Ag_2CrO_4) begins after 0.50 mL of K_2CrO_4 have been added. What is the K_{sp} for Ag_2CrO_4 ?
13. In attempting to precipitate silver chloride, $K_{\text{sp}} = 1.7 \times 10^{-10}$, Jill Student adds 50.0 mL of 0.10 M NaCl solution to 50.0 mL of 0.050 M AgNO_3 solution.
- How many milligrams of $\text{AgCl}(s)$ are precipitated?
 - What is the final $[\text{Ag}^+]$ in the solution?
14. Calcium fluoride, CaF_2 , has $K_{\text{sp}} = 3.4 \times 10^{-11}$. CaF_2 will be used to fluoridate a municipal water supply in a hard-water area where $[\text{Ca}^{2+}] = 0.070\text{ M}$. What is the maximum F^- concentration, in mol L^{-1} , that can be achieved in this area by dissolving CaF_2 ?
15. Silver hydroxide, AgOH , has $K_{\text{sp}} = 2 \times 10^{-8}$.
- What is the pH of a saturated solution of AgOH ?
 - What is the maximum pH possible for a solution in which $[\text{Ag}^+] = 0.50\text{ M}$?
16. Ferric hydroxide, $\text{Fe}(\text{OH})_3$, is extremely insoluble, with $K_{\text{sp}} = 1.0 \times 10^{-38}$. What is the maximum pH that is possible in a solution of $[\text{Fe}^{3+}] = 0.10\text{ M}$ before $\text{Fe}(\text{OH})_3$ precipitates?

3.3 Weak Acids and Bases

OBJECTIVES

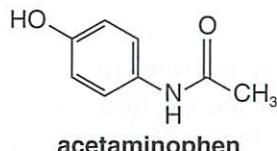
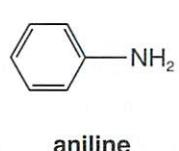
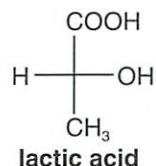
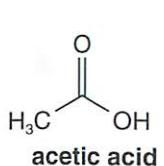
After studying this topic, you should be able to:

- Explain the differences between the Arrhenius, Brønsted-Lowry, and Lewis acid-base theories.
- Predict the acid-base behaviour of a compound based on its structure.
- Identify conjugate species of acids and bases.
- Perform calculations using equilibrium constants for various weak acid and weak base solutions.
- Predict the acid-base properties of salt solutions and determine their pH.
- Use structural factors to predict the relative strengths of weak acids.

INTRODUCTION

Acids are often defined as substances that increase hydrogen ion concentration, $[H^+]$, in solution, while bases are often defined as those substances that increase hydroxide ion concentration, $[OH^-]$, in solution. The terms *strong* and *weak* are used to describe the behaviour of acids and bases, and have nothing to do with “hole burning” power or acid/base concentration. Strong acids and bases completely ionize in solution, whereas weak acids and bases do not ionize completely. Weak acid and weak base reactions proceed until an equilibrium is achieved between the reactants and products.

Weak acids and weak bases are encountered almost everywhere. Acetic acid, for example, is a well-known weak acid formed during the fermentation of ethanol. At approximately 5% to 8% concentration by volume, it is sold worldwide as table vinegar; at higher concentrations it is used in home and commercial food pickling. Lactic acid is a weak acid prevalent in sour dairy products, sausages, and fermenting fruit and vegetables. It is found in most living organisms, including bacteria, and has been consumed by humans throughout history. Lactic acid is also a by-product of anaerobic energy production in muscle tissue and has a crucial role related to the supply of that energy. Acetaminophen, an analgesic, is another weak acid.



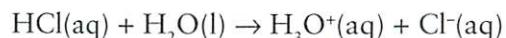
Ammonium hydroxide (NH_4OH) solution is a common weak base and among other things, is an effective cleaning product (pungent odour notwithstanding). Another important weak base, aniline, is used in the production of commercial dyes, polyurethane, and acetaminophen. In this topic, the behaviour of weak acids and bases is examined.

ACID–BASE TERMINOLOGY

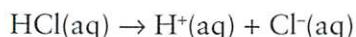
Strong Acids and Bases

As previously mentioned, strong acids and bases are those that completely ionize in solution. Acids increase $[\text{H}^+]$ while bases increase $[\text{OH}^-]$. Since H^+ is really just a proton, it cannot exist in solution as such. Thus when an acid is in an aqueous solution, the H^+ released from the acid combines with water to form H_3O^+ . However, for convenience, the terms H^+ and H_3O^+ are used interchangeably.

HCl is an example of a strong acid. When dissolved in water, 1 mol HCl produces 1 mol H^+ (H_3O^+) and 1 mol Cl^- :



Often, the water in this equation is omitted and the equation is simply written as:



with the (aq) designation indicating that the reaction takes place in water. Other examples of strong acids include HBr , HI , HNO_3 , HClO_4 , and H_2SO_4 .



NaOH is an example of a strong base. 1 mol of NaOH provides 1 mol of Na^+ and 1 mol of OH^- as shown in the following equation:



Other examples of strong bases include KOH, Mg(OH)_2 , and Ca(OH)_2 .

Arrhenius and Brønsted-Lowry Acids and Bases

In the equations above, a unidirectional arrow (\rightarrow) was used to indicate that the reactions proceed completely to the product side. In other words, strong acids and bases ionize completely in solution.

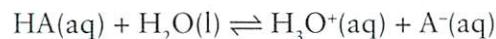
The two examples above also illustrate the Arrhenius theory of acids and bases, which states:

- An acid produces H_3O^+ ions in water.
- A base produces OH^- ions in water.

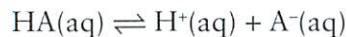
The Brønsted-Lowry theory of acid–base behaviour is more general than the Arrhenius theory, and is especially useful for weak acids and bases:

- An acid is a proton donor.
- A base is a proton acceptor.

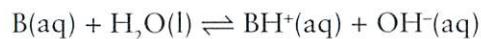
Recall that weak acids and bases do not ionize completely in solution; the reactions proceed until an equilibrium is achieved between reactants and products. When a weak acid (HA) ionizes, it donates a hydrogen ion to water (proton donor) as shown in the equilibrium reaction below.



The weak acid equilibrium equation is often simplified to:



When a weak base (B) ionizes, it accepts a hydrogen ion (proton acceptor) from water or another compound acting as an acid. The weak base equilibrium reaction is written as:

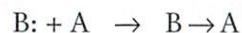


For weak acids, the subscript ‘a’ is added to the equilibrium constant symbol, which becomes K_a . For weak bases, the subscript ‘b’ is added and the equilibrium constant symbol becomes K_b .

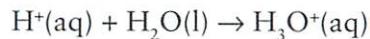
Lewis Acids and Bases

The Arrhenius and Brønsted-Lowry definitions of acids and bases are very useful for many applications. In some cases, however, it is advantageous to generalize the concept of acids and bases to include even those reactions where no H^+ and OH^- species are involved. This generalization was proposed by Gilbert Lewis.

A *Lewis acid* is a substance that can accept a pair of electrons from another atom to form a bond. A *Lewis base* is a substance that donates a pair of electrons to another atom to form a bond. The species formed in this reaction is called an acid–base *adduct* as shown in the generic equation:



where A represents the acid, B represents the base and $B \rightarrow A$ represents the acid–base adduct. Note that in this context, the arrow in $B \rightarrow A$ indicates the species donating the pair of electrons (it is not a reaction arrow). The reaction between the hydrogen ion and water is of this type:

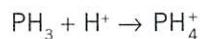


Here, the hydrogen ion acts as a Lewis acid, the water (with two nonbonding pairs of electrons on the oxygen) acts as a Lewis base, and the hydronium ion is the adduct.

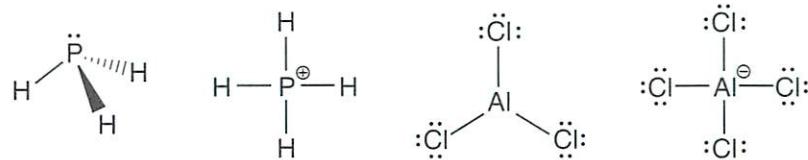


Example 3.3.1. Identifying Lewis Acids and Bases

Identify PH_3 and AlCl_3 as either a Lewis acid or a Lewis base in the following reactions:

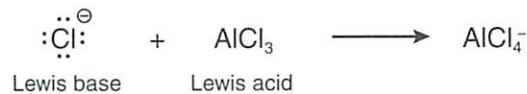


Solution: The Lewis structure for each molecule is shown below:

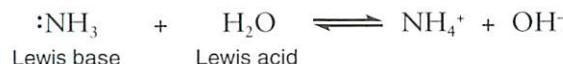


The phosphorous atom in PH_3 bears a nonbonding pair of electrons, which is used to form a bond in PH_4^+ . Hence PH_3 is a Lewis base.

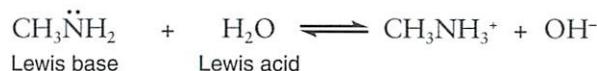
In AlCl_3 the central Al atom has an incomplete octet. It readily accepts electrons from another species and in doing so, acts as a Lewis acid:

**Ammonia and Amines**

The nitrogen atom of NH_3 carries a nonbonding pair of electrons. Therefore, the NH_3 molecule can act as a Lewis base. In particular, when ammonia reacts with water, the nonbonding pair of electrons attracts the partially positive hydrogen of water and, in the subsequent reaction, forms a new N–H bond. The overall reaction is

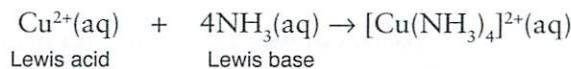


Amines may be viewed as ammonia molecules in which one or more of the H atoms are substituted by alkyl groups. The simplest amine is methylamine, CH_3NH_2 . The reaction of amines with water is analogous to that of ammonia. For example, methylamine reacts with water as follows:



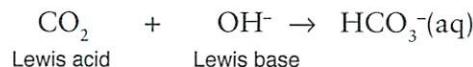
Metal Cations

Metal cations are another group of species that can act as Lewis acids. These ions form complex ions, known as *coordination complexes*, when they react with Lewis bases such as water (H_2O), ammonia (NH_3), or the hydroxide ion (OH^-). For example:



Oxides of Nonmetals

Some compounds, especially the oxides of nonmetals, behave as Lewis acids when they react with hydroxide. For example, carbon dioxide (CO_2) reacts with OH^- to form bicarbonate (HCO_3^-),

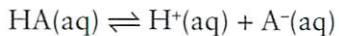


This reaction is currently investigated as a potential method to remove carbon dioxide from the atmosphere.

EQUILIBRIUM CONSTANTS, pH, AND PERCENT IONIZATION

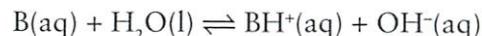
Weak acid and weak base equilibrium reactions are governed by the equilibrium constant expression, K , with subscripts a for weak acids and b for weak bases.

For HA (weak acid):



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

For B (weak base):



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$



Recall that the magnitude of the equilibrium constant is a measure of the extent of the forward reaction: if $K > 1$, the equilibrium lies to the right and if $K < 1$, the equilibrium lies to the left.

In the case of weak acids and bases, their K_a and K_b values are, by definition, much less than one. Some weak acids and bases are stronger than others, and this is reflected in their respective K_a or K_b values (the larger the K value, the greater the ionization).

For example, acetic acid (CH_3COOH) is a weak acid ($K_a = 1.8 \times 10^{-5}$), and trichloroacetic acid (CCl_3COOH) is a much stronger weak acid ($K_a = 2.0 \times 10^{-1}$). Note that CCl_3COOH is a stronger weak acid, but it still isn't a strong acid. “Stronger” merely refers to the fact that it ionizes to a greater extent.

Similarly, ammonia (NH_3) is a weak base ($K_b = 1.8 \times 10^{-5}$), and methylamine (CH_3NH_2) is a slightly stronger weak base ($K_b = 6.4 \times 10^{-4}$).

K_a and K_b values are often expressed using a logarithmic scale as follows:

$$\text{p}K_a = -\log K_a \text{ and } \text{p}K_b = -\log K_b$$

Thus for acetic acid: $\text{p}K_a = 4.74$, and for trichloroacetic acid: $\text{p}K_a = 0.70$

A comparison of the $\text{p}K_a$ values for the two acids above shows that the numerical value of $\text{p}K_a$ becomes smaller as the strength of the acid (K_a) increases. The K_a and K_b for a selection of weak acids and bases, along with the corresponding $\text{p}K_a$ and $\text{p}K_b$ values, are shown in Table 3.3.1 and Table 3.3.2, respectively.

Although all weak acids have K_a values that are much less than one, weak acids vary considerably in strength. Some weak acids are stronger (larger K_a), while others are weaker (smaller K_a). Therefore, “stronger” and “weaker” are relative terms.

weaker weak acid
smaller K_a (larger $\text{p}K_a$)

stronger weak acid
larger K_a (smaller $\text{p}K_a$)

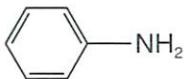
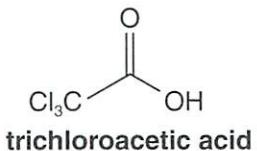
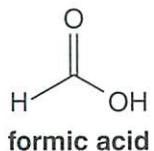
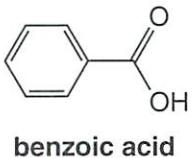
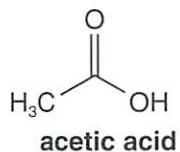


TABLE 3.3.1 EQUILIBRIUM CONSTANTS FOR SELECTED
BRØNSTED-LOWRY WEAK ACIDS

WEAK ACID	K_a	pK_a
Hydrocyanic acid, HCN	4.0×10^{-10}	9.40
Hypochlorous acid, HClO	3.5×10^{-8}	7.46
Acetic acid, CH_3COOH	1.8×10^{-5}	4.74
Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}	4.20
Formic acid, HCOOH	1.9×10^{-4}	3.72
Nitrous acid, HNO_2	4.5×10^{-4}	3.35
Hydrofluoric acid, HF	6.7×10^{-4}	3.17
Trichloroacetic acid, Cl_3CCOOH	2.0×10^{-1}	0.70

TABLE 3.3.2 EQUILIBRIUM CONSTANTS FOR SELECTED
BRØNSTED-LOWRY WEAK BASES

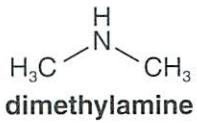
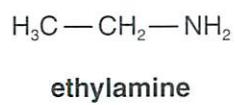
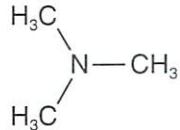
WEAK BASE	K_b	pK_b
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	7.4×10^{-10}	9.13
Pyridine, $\text{C}_5\text{H}_5\text{N}$	1.5×10^{-9}	8.82
Ammonia, NH_3	1.8×10^{-5}	4.74
Trimethylamine, $(\text{CH}_3)_3\text{N}$	7.4×10^{-5}	4.13
Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$	4.3×10^{-4}	3.37
Methylamine, CH_3NH_2	6.4×10^{-4}	3.19
Dimethylamine, $(\text{CH}_3)_2\text{NH}$	7.4×10^{-4}	3.13



aniline



pyridine



Weak Acid and Weak Base Calculations

Determination of the pH for solutions of strong acids and strong bases was straightforward (see the General Review in Chem 1301A). Because dissolved strong acids and strong bases are completely ionized, the concentration of H^+ in a solution of a strong acid is simply the total concentration of the acid times the number of protons in each acid molecule. Similarly, the concentration of OH^- in a solution of a strong base such as NaOH is the total concentration of NaOH.

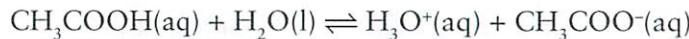
Determination of the pH for solutions of weak acids and bases is more involved because only a fraction of the dissolved molecules will ionize to form H^+ (acid) or OH^- (base).

The method for determining the pH for solutions of weak acids and weak bases is explained below. Note that the following three relations still apply:

$$\text{pH} = -\log[\text{H}^+] \quad \text{pOH} = -\log[\text{OH}^-] \quad \text{pH} + \text{pOH} = 14$$

pH and Percent Ionization of Weak Acids

The K_a for acetic acid (CH_3COOH) is 1.8×10^{-5} . In a solution of CH_3COOH the initial concentration may be represented by c , and the amount of CH_3COOH that ionizes may be represented by x because it is in a 1:1 ratio. The concentrations of H^+ and CH_3COO^- that result from this ionization are also represented by x . The equilibrium for this reaction is written as:



Initial:	c	0	0
Equilibrium:	$c - x$	x	x

The equilibrium constant expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{c-x}$$

To solve for x , $K_a = \frac{x^2}{c-x}$ has to be expanded into a quadratic equation:

$$x^2 + K_a x - K_a c = 0$$

which corresponds to $ax^2 + bx + d = 0$ and can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ad}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2}$$

Because of the \pm sign, the quadratic formula will give two values of x , but only a positive concentration is possible.

If the initial concentration (denoted by c) of CH_3COOH is 0.100 M , this value and the value of K_a may be substituted into the quadratic formula.

The result is: $x = 1.33 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$, and the $\text{pH} = 2.875$



Percent ionization, α , is the amount of the weak acid ionized (or dissociated) expressed as a percent of the original concentration of the acid, using the relationship:

$$\alpha = \frac{x}{c} \times 100\%$$

Therefore, in this example $\alpha = \frac{1.33 \times 10^{-3}}{0.100} \times 100\% = 1.33\%$.

To simplify the arithmetic, if α is less than 5%, the approximation that x is much smaller than c is used. This makes $c - x \approx c$ and therefore:

$$K_a \approx \frac{x^2}{c} \text{ or } x = \sqrt{cK_a} = [\text{H}_3\text{O}^+]$$

With $c = 0.100 \text{ M}$ and $K_a = 1.8 \times 10^{-5}$, $x = [\text{H}_3\text{O}^+] = 1.342 \times 10^{-3} \text{ M}$ and the pH = 2.872. The percent ionization in this case is 1.342%.

When the two results in the example are compared, it is apparent that there is little difference between the exact answer obtained using the quadratic formula and the answer obtained using the approximation. In fact, the “error” in the approximated answer is less than 1%. Using the simpler method will save time, but there may be instances where the approximation will be poor. How does one know when it is OK to use the approximation $c - x \approx c$? You may use either of the following tests.

1. Calculate the ratio for c/K_a . If the result is greater than about 400, then the approximation $c - x \approx c$ is acceptable. If the result is less than 400, then the approximation is too crude and the quadratic formula should be used.
2. If α is less than 5%, the approximation $c - x \approx c$ is acceptable. This test is less helpful, however, because you normally do not know α until after you have solved for x .

If the equilibrium concentrations of all species are known, a value for K_a may be calculated. It is also possible to calculate the initial concentration of the weak acid. For these calculations, the exact form of the equilibrium constant expression should always be used. Simply put: Do not neglect x with respect to c if you know what x is. In other words, if you know x , use it!

Example 3.3.2. Percent Ionization and K_a of a Weak Acid (In-Class Exercise)

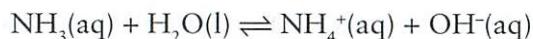
A 0.0250 M solution of a weak acid, HA, has a pH of 2.75. Determine the percent ionization of the acid and its K_a .

Example 3.3.3. Concentration of Nitrous Acid (In-Class Exercise)

Nitrous acid, HNO_2 , has $K_a = 4.5 \times 10^{-4}$. Determine the initial concentration of HNO_2 if a solution of this acid has a pH of 3.65.

pH and Percent Ionization of Weak Bases

Up to this point, the focus has been on the ionization of weak acids. The same principles apply to the reactions of weak bases with water. Consider a solution of 0.100 M NH_3 . The K_b for NH_3 is 1.8×10^{-5} . The equilibrium is written as:



Equilibrium: $c - x$ x x

$$\text{and } K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{c-x}$$

Solving for x using the K_b expression follows the same steps as solving for x using the K_a expression. (The approximation that $c - x \approx c$ can be made, etc.)

When solving for x using the K_b expression, the $[\text{OH}^-]$ is determined. Therefore, if the pH of the solution is required, it can be calculated from the pOH.

Example 3.3.4. Concentration and Percent Ionization of Methylamine (In-Class Exercise)

A solution of methylamine (CH_3NH_2) has a pH of 10.45 and the K_b for $\text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}$. Calculate the initial concentration of methylamine and the % ionization of methylamine.

Effect of Dilution on Percent Ionization

The results contained in the previous “Methylamine” In-Class Exercise example indicate that for a solution of CH_3NH_2 with an initial concentration of $4.06 \times 10^{-4} \text{ M}$, the percent ionization is 69.4%. If the initial concentration of CH_3NH_2 was 0.400 M, the percent ionization is 4.0% and the pH of the solution is 12.20. A comparison of these results seems to indicate that the more dilute the solution of a weak acid or base, the greater the *percent* ionization.

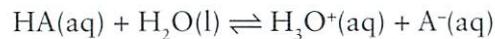
Because the K_a or K_b for the weak acid or base does not change, there must be changes to the concentrations of the products at equilibrium when the initial concentration of acid or base is decreased by dilution. This trend is shown in Table 3.3.3 for HF. Be sure to understand the chemical basis behind this trend.

TABLE 3.3.3 EFFECT OF DILUTION ON PERCENT IONIZATION AND pH

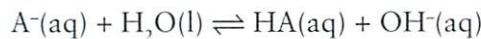
INITIAL [HF]	EQUILIBRIUM $[H^+]$	α	pH
1.0	2.6×10^{-2}	2.6%	1.59
0.10	7.9×10^{-3}	7.9%	2.10
0.010	2.3×10^{-3}	22%	2.64

CONJUGATE SPECIES

The *conjugate base* of an acid is the species formed when the acid has donated a proton. Conversely, the *conjugate acid* of a base is the species formed when the base has accepted a proton. For example, in the equation describing the ionization of a weak acid in solution:



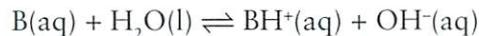
A^- is the *conjugate base* of the weak acid HA. The conjugate base will behave like a weak base when in solution:



This solution will be basic due to the hydroxide ion produced in the reaction. As this is an equilibrium reaction, the conjugate base will have an equilibrium constant expression:

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Similarly, in the equation describing the dissociation of a weak base B,



the species BH^+ is the *conjugate acid* of the weak base B. The conjugate acid will behave like a weak acid in solution:



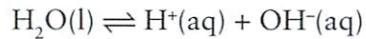
and will have an equilibrium constant expression:

$$K_a = \frac{[H_3O^+][B]}{[BH^+]}$$

This solution will be acidic due to the hydronium ion produced in the reaction.

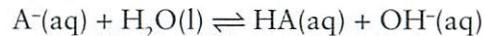
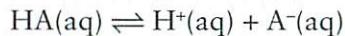
Equilibrium Constant K_w

The equilibrium constant for the ionization of water:

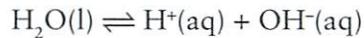


is $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C).

Now consider the ionization equilibria of a weak acid (HA) and its conjugate base:



There is an important relationship between the K_a for a weak acid and K_b for its conjugate base. Addition of the two equations above yields:



When two equations are added, the equilibrium constants are multiplied in order to determine the equilibrium constant for the resultant equation. Therefore:

$$K_a \times K_b = K_w$$

and this result holds for any conjugate acid–base pair. (K_w is also known as the *ion product of water*.) Another way to illustrate the K_a , K_b , and K_w relationship is:

$$K_w = K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-]$$

$$\text{Alternatively: } pK_a + pK_b = 14$$

The relationship between equilibrium constants shows that the stronger the weak acid is, the weaker the weak conjugate base will be. Acetic acid, for example, has $K_a = 1.8 \times 10^{-5}$ while its conjugate base (the acetate ion) has a $K_b = 5.6 \times 10^{-10}$. Formic acid is stronger (has a larger K_a value) than acetic acid, so it follows that formate is a weaker base than acetate.

By the same token, strong acids have extremely weak conjugate bases. In fact, their bases are so weak that they are called *spectator ions* and do not affect pH at all. When HCl ionizes, the Cl⁻ produced is a spectator ion.

Salts

A salt is an ionic solid containing cations (other than just H⁺) and anions. When a salt dissolves in water, its cation and anion separate from each other. The salt may not be very soluble, but whatever dissolves is completely ionized.

Cations that do not have any effect on pH (i.e., do not react with water) are spectator ions. Most monovalent and divalent metal ions such as Li⁺, Na⁺, K⁺, Ca²⁺, and Ba²⁺ act as spectator ions. Similarly, many anions act as spectator ions and do not affect pH. This is the case for the conjugate bases of strong acids (Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, SO₄²⁻). Some cations, such as NH₄⁺ and related ammonium species, act as weak acids:

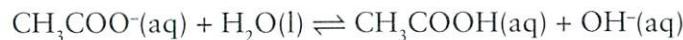


NH₄⁺ is the conjugate acid of the weak base NH₃; therefore, a solution of ammonium chloride (NH₄Cl) is acidic.

Anions that are the conjugate bases of weak acids act as weak bases (F⁻, CO₃²⁻, etc.). For example, sodium acetate (CH₃COONa) will ionize in water according to:



Because CH₃COO⁻ is the conjugate base of CH₃COOH and, as stated, Na⁺ ions have no effect on pH, it follows that a solution of CH₃COONa will be basic due to the reaction of acetate, CH₃COO⁻, with water (hydrolysis):



In the examples considered so far, only one of the ions had an effect on pH, while the other one was a spectator ion. What if the cation AND anion can affect the pH? If $K_a > K_b$, the salt is acidic. A solution of NH₄F is acidic:

$$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}; K_b(\text{F}^-) = 1.4 \times 10^{-11}$$

Conversely, if $K_b > K_a$ the salt is basic. A solution of NH₄ClO is basic:

$$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}; K_b(\text{ClO}^-) = 3.6 \times 10^{-7}$$

A similar argument can be used to decide if an *amphiprotic anion* (a species that can act as both an acid or a base) will be acidic or basic.



A solution of NaHCO_3 (sodium bicarbonate or baking soda) is basic since $K_b > K_a$. This is why NaHCO_3 is often used to neutralize acid spills.

Calculations with Conjugate Species and Salts

Because a conjugate base behaves like a weak base, and a conjugate acid behaves like a weak acid, the approach to finding the pH (or other properties) of these solutions is similar to the examples already shown. However, it may be necessary to determine which, if any, species will set up an equilibrium.

Example 3.3.5. pH of KCN (In-Class Exercise)

Determine the pH of a 0.100 M solution of KCN.

Data: K_a for HCN = 4.0×10^{-10}

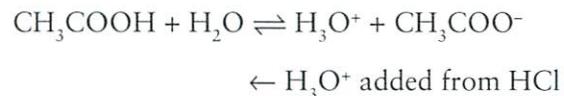
Example 3.3.6. Determination of K_a from pH of Salt (In-Class Exercise)

A 0.285 M solution of the sodium salt, NaA, of the weak monoprotic acid, HA, has a pH of 9.65. Determine K_a for the acid HA.

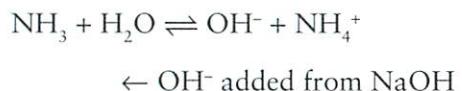
THE COMMON ION EFFECT

The effect of a *common ion* with respect to the solubility of an ionic solid was previously discussed in the *Solubility of Ionic Compounds* section. The common ion effect may also come into play when discussing the ionization of weak acids and bases. In this section, the effect of an additional source of H_3O^+ (in the case of acids) or OH^- (in the case of bases) on the ionization of a weak acid or base is examined.

In a solution of a weak acid and a strong acid, there are two sources of the H_3O^+ ion. For example, if a strong acid such as HCl is added to a weak acid such as CH_3COOH , both the HCl and CH_3COOH produce H_3O^+ . The H_3O^+ is therefore a common ion. In the equilibrium reaction shown below, when H_3O^+ is added the equilibrium shifts in the reverse direction and the concentration of the anion, CH_3COO^- , is reduced. This is known as the *common ion effect* and is really just an example of Le Châtelier's principle. Note that the amount of H_3O^+ produced by the dissociation of the weak acid is negligible when compared to that produced by the strong acid.



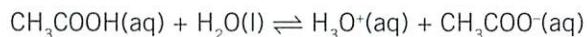
In a similar fashion, when a strong base such as NaOH is put in solution with a weak base such as NH_3 , the addition of the common ion OH^- shifts the equilibrium in the reverse direction, away from NH_4^+ production.



Example 3.3.7. Common Ion Effect

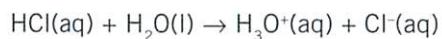
Determine the pH and percent ionization of a 0.10 M CH_3COOH solution ($K_a = 1.8 \times 10^{-5}$) that also contains 0.050 M HCl.

Solution: First consider the equilibrium without the HCl:



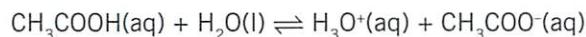
Initial:	0.10	0	0
Equilibrium:	$0.10 - x$	x	x

Now consider the equation for the ionization of HCl:



Initial:	0.050	0	0
After:	0	0.050	0.050

The easiest way to deal with the addition of the HCl is to assume that the H_3O^+ is present in the solution before the CH_3COOH starts to ionize. Since the initial concentration of $\text{CH}_3\text{COO}^-(\text{aq})$ is 0, the reaction must proceed to the right.



Initial:	0.10	0.050	0
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Equilibrium:	0.10 - x	0.050 + x	x
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The equilibrium constant expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Substituting the equilibrium concentrations:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.050 + x)(x)}{0.10 - x}$$

Inspection of the initial concentration of the weak acid and K_a indicates that the approximation $0.10 - x \approx 0.10$ is valid. Can the same be said about the concentration of H_3O^+ ? Is it safe to say that $0.050 - x \approx 0.050$? Since there is no mathematical test that can be performed, a little logic is required. If the approximation $0.10 - x \approx 0.10$ is valid, then x must be a small number. The presence of the common ion means that even less weak acid will ionize. Therefore, x is smaller in the presence of a common ion. It follows then that the approximation $0.050 - x \approx 0.050$ is valid.

The equilibrium constant expression is now simplified:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.050)(x)}{0.10}$$

$$\text{So } x = 3.6 \times 10^{-5} \text{ M} = [\text{CH}_3\text{COO}^-]$$

Note that in this example, $x \neq [\text{H}_3\text{O}^+]$ because there is also H_3O^+ present from the ionization of HCl. Strictly speaking, $[\text{H}_3\text{O}^+] = 0.050 + 3.6 \times 10^{-5}$, but it should be apparent that the small amount of H_3O^+ that is produced by the ionization of CH_3COOH is negligible with respect to 0.050 M.

If $[\text{H}_3\text{O}^+] = 0.050$, then $\text{pH} = 1.30$. To solve for percent ionization, the expression is:

$$\alpha = \frac{x}{c} \times 100\% = \frac{3.6 \times 10^{-5}}{0.10} \times 100\% = 0.036\%$$

Compare this result with the percent ionization calculated for the 0.100 M solution of CH_3COOH in water (1.33%). The difference in the two results clearly shows the effect of the common ion — it suppresses the ionization of the weak acid quite dramatically. As with all previous examples, what holds true for a weak acid will also hold true for a weak base. Adding a strong base will suppress the ionization of the weak base.

POLYPROTIC WEAK ACIDS

Some weak acids are *polyprotic*, which means that they contain more than one ionizable hydrogen atom. When these acids ionize, they do so in stages, each with a different K_a value. One example is the weak *diprotic* acid, carbonic acid (H_2CO_3):



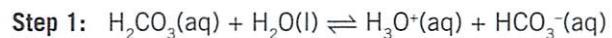
Note that K_{a1} is quite a bit larger than K_{a2} . This means that the amount of H_2CO_3 ionized is considerably greater than the amount of HCO_3^- dissociated. It follows, then, that although H_3O^+ is produced in both steps, the pH of the solution is overwhelmingly due to the H_3O^+ produced in the first step. K_{a2} is much smaller because the conjugate base from the second ionization has two negative charges and is therefore less stable than the conjugate base from the first ionization.

This is an example of a simultaneous equilibria (both reactions are happening at the same time). As a result, both the bicarbonate ion (HCO_3^-) and the carbonate ion (CO_3^{2-}) are present in the equilibrium mixture. In order to determine the equilibrium concentrations of these species, each equilibrium must be analyzed separately.

Example 3.3.8. pH of H₂CO₃ Solution

Find the pH, [HCO₃⁻], and [CO₃²⁻] for a 0.250 M solution of H₂CO₃ with the K_a values from above.

Solution: This is a diprotic acid, so each step must be considered separately.



Initial: 0.250 0 0

Equilibrium: 0.250 - x x x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.2 \times 10^{-7} = \frac{x^2}{0.250 - x}$$

Comparing 0.250 and K₁ shows that the approximation 0.250 - x ≈ 0.250 is valid, so solving for x gives:

$$x = \sqrt{0.250 \times 4.2 \times 10^{-7}} = 3.24 \times 10^{-4} = [\text{H}_3\text{O}^+] = [\text{HCO}_3^-]$$

The percent ionization in Step 1: $\alpha = \frac{3.24 \times 10^{-4}}{0.250} \times 100\% = 0.13\%$

Step 2: In the second step, the equilibrium is set up the same way as in Step 1, but the initial concentrations used in Step 2 are the equilibrium concentrations of those species determined in Step 1. In Step 2, the variable y is used to denote the amount of HCO₃⁻ ionized.



Initial: 3.24 × 10⁻⁴ 3.24 × 10⁻⁴ 0

Equilibrium: 3.24 × 10⁻⁴ - y 3.24 × 10⁻⁴ + y y

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.8 \times 10^{-11} = \frac{(3.24 \times 10^{-4} + y)(y)}{3.24 \times 10^{-4} - y}$$

This is another example of a common ion equilibrium (H₃O⁺ is common to both Step 1 and Step 2). The concentration of this common ion is the sum of the amounts produced in both steps:

3.24 × 10⁻⁴ from Step 1 and y from Step 2.

Due to the common ion effect, the value of y will be quite small, even relative to 3.24×10^{-4} . The approximation $3.24 \times 10^{-4} - y \approx 3.24 \times 10^{-4}$ may therefore be used. This approximation can be validated by comparing the initial concentration of HCO_3^- and K_{a2} from Step 2.

If the approximation that $3.24 \times 10^{-4} - y \approx 3.24 \times 10^{-4}$ is valid, then the approximation that $3.24 \times 10^{-4} + y \approx 3.24 \times 10^{-4}$ must also be valid.

$$\text{Therefore: } 4.8 \times 10^{-11} = \frac{(3.24 \times 10^{-4})(y)}{3.24 \times 10^{-4}} = y = [\text{CO}_3^{2-}]$$

Note that this is a general result for a weak polyprotic acid. The concentration of the 2⁻ species (CO_3^{2-} in this case) is numerically equal to K_{a2} . No calculation is needed.

$$\text{The percent ionization in Step 2: } \alpha = \frac{4.8 \times 10^{-11}}{3.24 \times 10^{-4}} \times 100\% = 1.48 \times 10^{-5}\%$$

The concentrations of all species at equilibrium are:

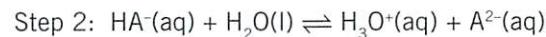
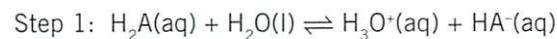
$$[\text{H}_2\text{CO}_3] = 0.250 \text{ M} - 3.24 \times 10^{-4} \text{ M} \approx 0.250 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.24 \times 10^{-4} \text{ M} + 4.8 \times 10^{-11} \text{ M} \approx 3.24 \times 10^{-4} \text{ M}$$

$$[\text{HCO}_3^-] = 3.24 \times 10^{-4} \text{ M} - 4.8 \times 10^{-11} \text{ M} \approx 3.24 \times 10^{-4} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

The results of these calculations lead to the following general statement about weak diprotic acids (H_2A) in water: For diprotic acids with $K_{a2} \ll K_{a1}$, the $[\text{A}^{2-}]$ is equal to K_{a2} , and the pH of the solution is primarily determined by the H_3O^+ obtained from the first ionization (Step 1).



Example 3.3.9. pH of Na_2CO_3 Solution (In-Class Exercise)

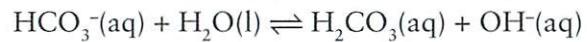
The method used for carbonic acid is also applicable to the conjugate bases of polyprotic acids that could only act as bases, that is, the conjugate base formed from the last ionization of the acid. Determine the pH of a 0.165 M solution of Na_2CO_3 . Use K_{a1} and K_{a2} for H_2CO_3 as required.

The previous examples involved a solution of H_2CO_3 , which could only act as an acid, and a solution of CO_3^{2-} , which could only act as a base. How about species such as HCO_3^- , which could act as a base and as an acid? Will a solution of NaHCO_3 (baking soda) be acidic or basic? When baking soda is dissolved in water, two reactions are possible.

If bicarbonate acts as an acid:



If bicarbonate acts as a base:



$$K_b \text{ of } \text{HCO}_3^- = \frac{K_w}{K_a \text{ of } \text{H}_2\text{CO}_3} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.38 \times 10^{-8}$$

A comparison of the K_a and K_b values for HCO_3^- shows that the K_b is approximately three orders of magnitude greater than the value of K_a . That is, HCO_3^- is much more likely to act as a base than as an acid. That is why solutions of sodium bicarbonate are frequently used in labs to neutralize acid spills, and also why baking soda reacts with vinegar!

Example 3.3.10. pH of KH_2PO_4 Solution (In-Class Exercise)

Predict whether a solution of potassium dihydrogen phosphate (KH_2PO_4) will be acidic or basic.

The K_a values for phosphoric acid, H_3PO_4 are:

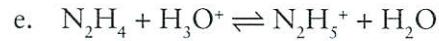
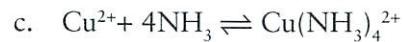
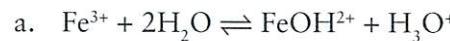
$$\text{H}_3\text{PO}_4 : K_{a1} = 7.1 \times 10^{-3}$$

$$\text{H}_2\text{PO}_4^- : K_{a2} = 6.3 \times 10^{-8}$$

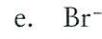
$$\text{HPO}_4^{2-} : K_{a3} = 4.5 \times 10^{-13}$$

Section 3.3 Review Problems

1. Identify the Lewis acid and base in each of the following reactions.



2. Identify the following molecules as Lewis acids and/or bases:



3. Determine the pH and percent ionization in the following aqueous solutions:



Each of the species in (a) through (d) above is one-half of a conjugate acid-base pair. In each case, provide the name and formula of the other half of the pair and calculate its K_a or K_b value.

4. What mass of propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, $pK_a = 4.87$, should be dissolved in water to 2.00 L volume in order to produce a pH of 2.50?

5. When acid HA is dissolved in water to 0.200 M concentration, the solution has a pH = 1.40. What is the K_a of this acid?

6. Hypochlorous acid, HOCl , is very weak, with $K_a = 3.5 \times 10^{-8}$. Calculate the value of $[\text{H}^+]$, the pH, and the percent ionization of this acid in concentrations of (a) 1.00 M (b) 0.0100 M.

Based on the results, indicate what happens to a weak acid solution on dilution: Does $[\text{H}^+]$ increase or decrease? Does the pH increase or decrease? Does the percent ionization increase or decrease?

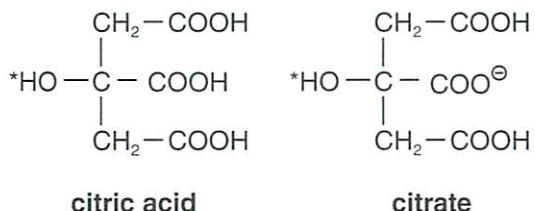
7. Trimethylamine, $(\text{CH}_3)_3\text{N}$, is an organic base slightly stronger ($K_b = 7.4 \times 10^{-5}$) than ammonia. Calculate the pOH, the pH, and the percent ionization of a 0.35 M solution.
8. For the following three weak acids: formic, HCOOH ($K_a = 1.9 \times 10^{-4}$), hydrofluoric, HF ($K_a = 6.7 \times 10^{-4}$), hydrogen oxalate ion, HC_2O_4^- ($K_a = 5.2 \times 10^{-5}$).
- Determine the pK_a value of each acid.
 - Arrange these three in order of decreasing acid strength.
 - Give the name and formula of the conjugate base of each acid.
 - Determine the K_b value of each conjugate base and arrange them in order of decreasing base strength.
9. A moderately weak acid is 25% ionized in 0.15 M concentration. What is its K_a value?
10. What mass of ammonia ($K_b = 1.8 \times 10^{-5}$) should be dissolved in water to 10 L volume in order to provide a pH of 11.18?
11. Determine the pH and percent hydrolysis in the following solutions (use K data from Tables 3.3.1 and 3.3.2).
 - 0.500 M potassium formate, HCOOK
 - 0.250 M ammonium bromide, NH_4Br
12. When 50.0 mL of 0.100 M $\text{NH}_3(\text{aq})$ ($K_b = 1.8 \times 10^{-5}$) solution is mixed with 20.0 mL of 0.250 M HCl solution, what is the pH after reaction?
13. When 0.020 mol of weak acid HA is dissolved in water to 100 mL volume, the ratio dissociated to undissociated, $[\text{A}^-] / [\text{HA}]$, at equilibrium is 0.30. What is the K_a of this acid?
14. 33.0 g of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is dissolved in water to 1.00 L volume. What is the pH of this solution? $\text{NH}_3(\text{aq})$ has $K_b = 1.8 \times 10^{-5}$.
15. What concentration of formic acid, HCOOH , ($K_a = 1.9 \times 10^{-4}$) in water would produce a pH of 4.5? What would the percent dissociation of the acid be in this solution?

16. Ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$, $K_b = 4.3 \times 10^{-4}$) and ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$, $K_b = 2.8 \times 10^{-4}$) are weak bases.

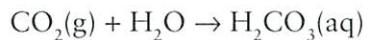
- Which of these is the stronger base?
- For the stronger base, calculate the pH and percent ionization in 0.50 M solution.

17. The acidity of lemon juice is due to the presence of citric acid, a triprotic acid ($M = 192 \text{ g mol}^{-1}$, $pK_{a1} = 3.1$). The pH of lemon juice is 2.3. Determine:

- The molar concentration of H^+ , citrate ion, and undissociated citric acid.
- The total molar concentration of citric acid, dissociated and undissociated.
- The percent ionization of citric acid.
- The mass percent of citric acid present (lemon juice density = 1.13 g mL^{-1}).



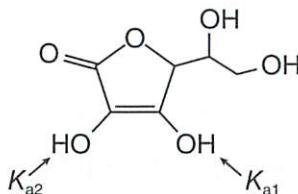
18. Carbonic acid is the result of dissolving CO_2 in water as follows:



It is a weak diprotic acid with $K_{a1} = 4.2 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$.

- Determine the pH, the concentration of all carbon-containing species, and the percent dissociation, first and second stages, in a solution of H_2CO_3 , concentration 0.100 M.
- Rainwater has a pH of about 5.6 resulting from the CO_2 dissolved from the atmosphere. What is the total concentration of all carbon containing species (H_2CO_3 , HCO_3^- , CO_3^{2-}), dissociated and undissociated, in rainwater?
- What volume of $\text{CO}_2(\text{g})$ has dissolved in each litre of rainwater to produce this acidity? (Take the molar volume as 22.4 L mol^{-1} .)

- d. What is the pH of an 0.100 M solution of sodium carbonate, Na_2CO_3 (washing soda)?
19. Vitamin C is a diprotic acid with $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$.



- a. What is the pH of a solution prepared by dissolving 10.0 g of ascorbic acid to make one litre of solution?
- b. What is the concentration of the doubly charged ascorbate anion in this solution?
20. A solution of sulfurous acid (diprotic) is prepared by dissolving 0.100 mol of SO_2 gas in 1.00 L of water, the reaction being:
- $$\text{SO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3(\text{aq})$$
- a. Write an equation for the first dissociation of H_2SO_3 .
- b. If the solution has $\text{pH} = 1.47$, what is the percent dissociation of the H_2SO_3 ?
- c. Determine K_{a1} for H_2SO_3 .
- d. If K_{a2} for this acid is 6.2×10^{-8} , what is the concentration of sulfite ion, $[\text{SO}_3^{2-}]$?

21. Determine the equilibrium concentrations of all species present for the equilibrium of a 0.150 M solution of the diprotic acid H_2SO_3 . What is the pH of the solution?

Data: $K_{a1} = 1.2 \times 10^{-2}$, $K_{a2} = 6.2 \times 10^{-8}$



■ 3.4 Buffer Solutions

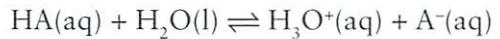
OBJECTIVES

After studying this topic, you should be able to:

- Identify the components needed to prepare a buffer solution.
- Determine whether a given set of components will create a buffer solution.
- Find the pH of a buffer solution, both before and after adding a strong acid or base.
- Identify the titration curves for a strong acid–strong base, strong acid–weak base, and weak acid–strong base by their respective shapes.
- Identify the buffer regions on titration curves.

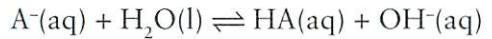
INTRODUCTION

Consider the behaviour of a weak acid in aqueous solution:



This solution is acidic due to the presence of H_3O^+ in the equilibrium mixture.

If a solution contains only A^- initially, the solution is basic due to hydrolysis. The conjugate base produces OH^- as follows:

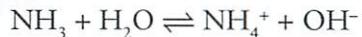


What happens if both the weak acid, represented by HA, and its conjugate base (in the form of a salt), represented by A^- , are present in the same solution? This type of solution is called a buffer solution. The outstanding feature of a buffer solution is its ability to withstand (or “buffer”) changes in pH when small amounts of a strong acid or base are added to it. In order for a solution to perform in this manner, it must meet some specific requirements, such as:

1. A buffer solution must contain a weak acid that will react with any OH^- ions (from a strong base) that may be added to the solution.

2. A buffer solution must also contain a weak base that will react with any H_3O^+ ions (from a strong acid) that may be added to the solution.
3. The acid and the base in the buffer solution must not react with each other; the only species that can possibly qualify are a weak acid or base and its own conjugate partner. In addition, the weak species and its conjugate partner must both be present in significant amounts. Buffers work best when there is about a 1:1 mixture of the weak species and its conjugate, but the solution will still perform its buffering function if the two concentrations are within a factor of 10.

If a solution contains *both* a weak acid and its conjugate base, they must be in equilibrium. Therefore, a buffer solution consists of a weak acid with its conjugate base behaving as a common ion, or a weak base with its conjugate acid behaving as a common ion.



PREPARING A BUFFER SOLUTION

The preparation of a buffer solution can be accomplished several ways, but the final solution must always contain a weak species and its conjugate partner. Note that if a buffer solution contains a weak acid and its conjugate base, the pH of that buffer will generally fall in the acidic range. Conversely, if the buffer solution contains a weak base and its conjugate acid, the pH of that solution will usually be basic.



Acid Buffer

A buffer solution composed of a weak acid and its conjugate base is often termed an acid buffer. For an acid buffer to be effective, both the weak acid (HA) and its conjugate base (A^-) must be present in significant and similar quantities. The easiest way to prepare this solution is to start with a solution of weak acid and add a salt that contains the conjugate base. This is shown in Figure 3.4.1 below:

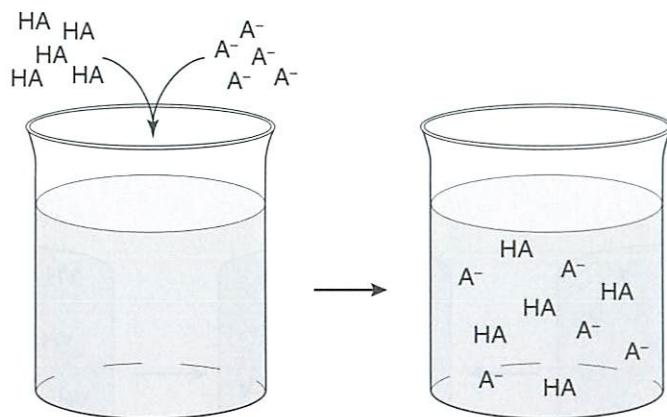
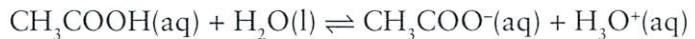


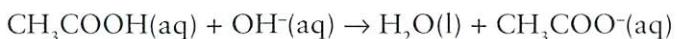
Figure 3.4.1

For example, 100 mL of a 0.150 M solution of acetic acid (CH_3COOH) plus about 1.25 g (0.0152 mol) of sodium acetate (CH_3COONa) is a buffer solution. The sodium acetate contains the acetate ion (CH_3COO^-), which is the conjugate base of acetic acid. The resultant solution will contain approximately 0.015 moles of each species. The equilibrium reaction is:



While the simplest method of preparing a buffer is to mix the two required species together, there are two other ways to make the previously described buffer solution. These involve starting with one of the two ingredients, and using a strong acid or strong base to create the other *in situ*.

Using acetic acid as an example, this is done by the reaction of acetic acid with hydroxide, thereby creating the acetate ion in the beaker.



The key is to use the correct amount of strong base to convert roughly half of the weak acid to its conjugate base. In the case of acetic acid, the number of moles of acetate ion, CH_3COO^- , formed is equivalent to the number of moles of hydroxide ion, OH^- , added.

This is shown in Figure 3.4.2 below:

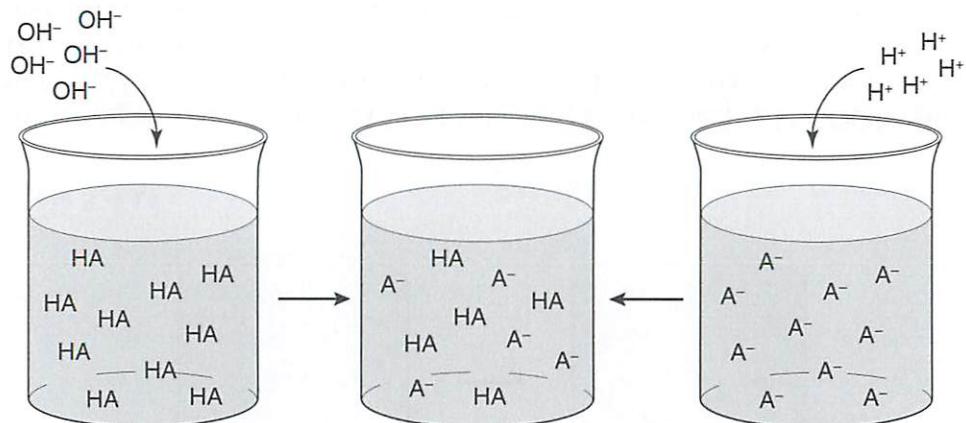
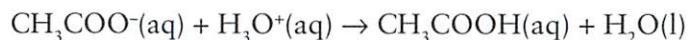


Figure 3.4.2

In a similar fashion, the same buffer can be created using strong acid to convert a conjugate base back to the weak acid. In the case of acetate ion and acetic acid, the strong acid HCl is added to sodium acetate, CH_3COONa , (a weak conjugate base) to form acetic acid, CH_3COOH , (the parent weak acid) in solution:



Again, it is important to convert approximately half of the acetate ions into acetic acid by reaction with HCl to form an effective buffer.

Base Buffer

Analogous combinations can be used for weak bases (B) and their conjugate acids (BH^+) to form base buffers. For example, suppose that 2.14 g (0.0400 mol) of ammonium chloride, NH_4Cl , are added to 250 mL of 0.160 M aqueous ammonia, NH_3 . The ammonia is a weak base and the ammonium ion, NH_4^+ , (from the NH_4Cl) is its conjugate acid, so the resultant solution will be a buffer solution, as both species are present in significant and roughly equivalent amounts (0.040 mol). This is shown in Figure 3.4.3 below:

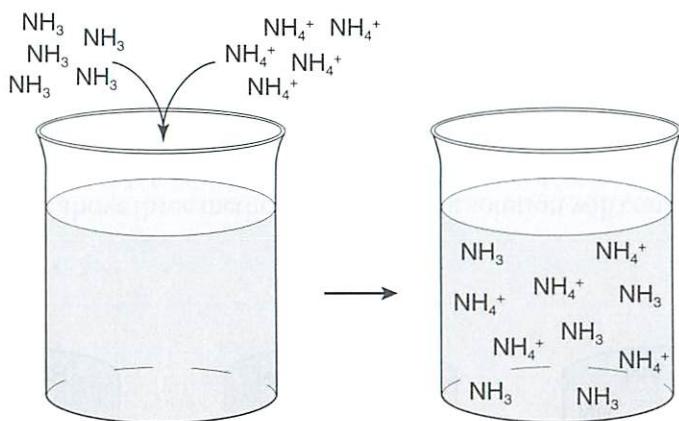
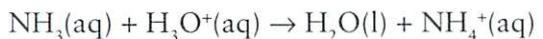
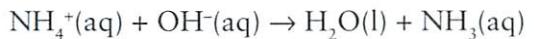


Figure 3.4.3

As was the case with weak acids, a reaction can also be used to produce the species required to form a buffer solution. That is, use a strong acid such as HNO_3 to convert roughly half of the base (NH_3) to its conjugate acid (NH_4^+):



Similarly, a strong base such as $NaOH$ can be added to convert approximately half of the conjugate acid (NH_4^+) back to the parent base (NH_3):



This is shown in Figure 3.4.4 below:

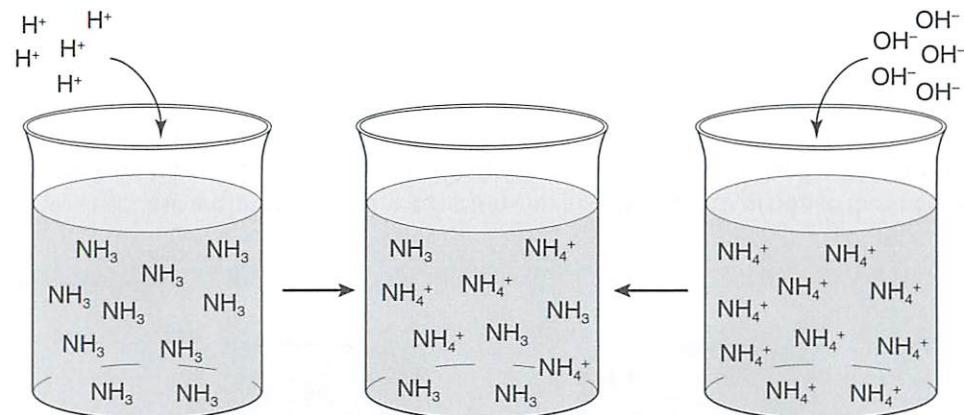


Figure 3.4.4

Using any of the above three methods, the resulting solution will consist of roughly equal amounts of weak base and its conjugate acid, producing a buffer solution.

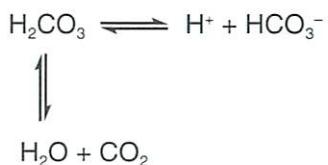
Example 3.4.1. Preparing Buffer Solutions (In-Class Exercise)

Determine which of the following combinations will produce a buffer solution.

- 0.15 mol HCOOH and 0.15 mol HCOOK
- 0.20 mol CH_3COOH and 0.20 mol KOH
- 0.10 mol CH_3COONa and 0.05 mol HCl
- 0.25 mol NH_4Cl and 0.10 mol NaOH
- 0.10 mol NH_3 and 0.10 mol HClO_4
- 0.35 mol CH_3NH_2 and 0.25 mol HNO_3

pH OF A BUFFER SOLUTION

The outstanding feature of a buffer solution is its ability to resist changes in pH. If it is essential that the pH of a solution remain nearly constant, a buffer solution is employed to accomplish this task. Human blood, with a pH of about 7.4, is an example of a buffered system. If small amounts of either acid or base make their way into the bloodstream, the pH does not change much. This is a good thing, as a change in blood pH of only 0.1 of a pH unit in either direction can be disastrous for a person's health. If a solution is to be used for buffering purposes, it is useful to calculate the pH of that solution.



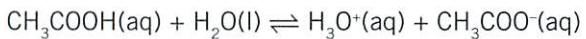
Example 3.4.2. pH of an Acetate Buffer

Calculate the pH of the resultant solution when 500 mL of 0.400 *M* CH₃COOH and 200 mL of 0.500 *M* CH₃COONa are mixed together.

Data: K_a for CH₃COOH = 1.8×10^{-5}

Solution: This solution contains both the weak acid, CH₃COOH, and its conjugate base, CH₃COO⁻, in comparable quantities. It should be recognized that this is a buffer solution and an example of the *common ion effect*. (The *common ion effect* was introduced in the *Solubility of Ionic Compounds* section.)

The equilibrium containing these two species may use the weak acid as the "reactant" with the conjugate base as the product, or vice versa. Either concept is valid, but it is much simpler to use the parent species as the reactant.



Before setting up the equilibrium, the molarities of both the CH₃COOH and the CH₃COO⁻ (which comes from the CH₃COONa) in solution after mixing must be found:

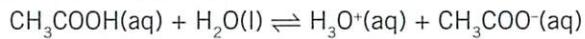
$$\text{Moles CH}_3\text{COOH} = 0.500 \text{ L} \times 0.400 \text{ M} = 0.200 \text{ mol}$$

$$\text{Moles CH}_3\text{COO}^- = 0.200 \text{ L} \times 0.500 \text{ M} = 0.100 \text{ mol}$$

$$\text{Molarity CH}_3\text{COOH} = \frac{0.200 \text{ mol}}{0.700 \text{ L}} = 0.286 \text{ M}$$

$$\text{Molarity CH}_3\text{COO}^- = \frac{0.100 \text{ mol}}{0.700 \text{ L}} = 0.143 \text{ M}$$

Now, set up the equilibrium as an example of a weak acid with the conjugate base acting as the common ion:



$$\text{Initial: } \quad 0.286 \text{ M} \quad \quad \quad 0 \quad \quad 0.143 \text{ M}$$

$$\text{Equilibrium: } 0.286 \text{ M} - x \quad \quad \quad x \quad \quad 0.143 \text{ M} + x$$

Note that the amount of CH₃COOH ionized is expressed as the variable x . This amount is equal to [H₃O⁺].

The equilibrium constant expression is:

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{\text{CH}_3\text{OOH}} = \frac{(x)(0.143+x)}{(0.286-x)}$$

In a buffer solution, the percent ionization is fairly small, often being just a percent or two. According to Le Châtelier's principle, if the acetate ion is added to the weak acid equilibrium, the reaction will proceed to the left. The value for x will be much smaller than in the weak acid solution alone. So, for a buffer solution, the value of x is *always negligible* when compared to the concentration of the parent or conjugate species.

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.143)}{(0.286)}$$

Therefore: $x = 3.6 \times 10^{-5} = [\text{H}^+]$, and the pH = 4.44.

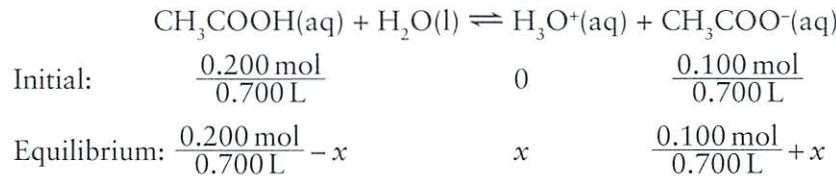
Note that the volume used to calculate molarity is the same for both species (they are both in the same solution). For buffer calculations, it is usually possible and often preferable to use mole amounts of the parent and conjugate species instead of concentration units. The other species (H₃O⁺ and OH⁻) must always be in concentration units (see example that follows).



There are two reasons why mole amounts work:

1. The parent and conjugate species are always in the same volume.
2. The value of x is always negligible when compared to the initial concentration of the parent and conjugate.

Revisiting the example:



$$K_a = 1.8 \times 10^{-5} = \frac{(x)\left(\frac{0.100 \text{ mol}}{0.700 \text{ L}} + x\right)}{\left(\frac{0.200 \text{ mol}}{0.700 \text{ L}} - x\right)}$$

with x negligible:

$$1.8 \times 10^{-5} = \frac{(x)\left(\frac{0.100 \text{ mol}}{0.700 \text{ L}}\right)}{\left(\frac{0.200 \text{ mol}}{0.700 \text{ L}}\right)}$$

The volumes cancel, thus: $1.8 \times 10^{-5} = \frac{(x)(0.100 \text{ mol})}{(0.200 \text{ mol})}$

Solving: $x = 3.6 \times 10^{-5} = [\text{H}^+]$, and the pH = 4.44.

Calculations for buffer solutions may therefore be carried out using moles or concentration units for the parent and conjugate. However, the parent and conjugate must be in the same units and, as previously stated, the H_3O^+ (for an acid buffer) and OH^- (for a base buffer) *must always be* in concentration units, M.

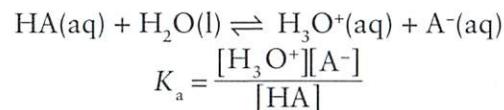
For a weak acid buffer, the equilibrium expression becomes:

$$K_a = \frac{[\text{H}_3\text{O}^+](\text{moles of conjugate base})}{(\text{moles of parent acid})}$$

This expression shows that the pH of a solution is dependent on the ratio of parent to conjugate species. Another outcome is that the volume of the solution is not a factor in determining pH. Thus, diluting a buffer solution does not change its pH.

The Henderson-Hasselbalch Method

A second method that is often used in solving buffer problems is the Henderson-Hasselbalch equation. Starting from the general form of the equilibrium reaction for a weak acid, HA, with water, the K_a expression is simply:



Taking the negative log of both sides results in:

$$-\log(K_a) = -\log\left(\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\right)$$

When terms are multiplied within a logarithm, they become added together when we separate the logarithm, resulting in:

$$-\log(K_a) = -\log[\text{H}_3\text{O}^+] - \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Then adding $\log([\text{A}^-]/[\text{HA}])$ to both sides gives:

$$-\log(K_a) + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log[\text{H}_3\text{O}^+]$$

$-\log[\text{H}_3\text{O}^+]$ is pH, and $-\log(K_a)$ is pK_a , which gives the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

However, as above, because concentrations are moles/volume:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{\left(\frac{n_{\text{A}^-}}{V_{\text{tot}}}\right)}{\left(\frac{n_{\text{HA}}}{V_{\text{tot}}}\right)}$$

and the Henderson-Hasselbalch equation can also be expressed as:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[n_{\text{A}^-}]}{[n_{\text{HA}}]}\right)$$

Using the Henderson-Hasselbalch equation, the K_a given in the question, and the moles found above, the solution to Example 3.4.2 becomes:

$$\text{pH} = 4.74 + \log\left(\frac{[0.100]}{[0.200]}\right)$$

or pH = 4.44.

As described in the *Preparing a Buffer Solution* section, there are many different ways to prepare a buffer solution. If the required pH of the solution is known, it is possible to work backward to determine the amount of reagents needed.

Example 3.4.3. Preparing a Buffer with a Given pH (In-Class Exercise)

What mass, in grams, of NaNO_2 must be added to 700 mL of 0.165 M HNO_2 to produce a solution with a pH of 3.50?

Data: K_a for $\text{HNO}_2 = 4.5 \times 10^{-4}$

Example 3.4.4. Base Buffers (In-Class Exercise)

The same principles may also be applied to base buffers. These solutions consist of a weak base and its conjugate acid.

A solution was prepared by adding 21.5 g of NH_4Cl to 1.50 L of 0.250 M NH_3 . Find the pH of this solution.

Data: K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$

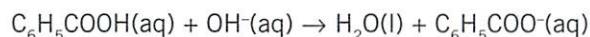
Buffer solutions can also be prepared using an acid–base reaction. Several examples of this type of reaction have already been discussed. An excess amount of some weak species (acid or base, parent or conjugate) is reacted with a strong acid or base. The reaction produces the second weak component necessary to produce a buffer solution.

Example 3.4.5. Buffers via an Acid–Base Reaction

100 mL of 0.500 M benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, $K_a = 6.3 \times 10^{-5}$, is mixed with 100 mL of 0.200 M NaOH. Find the pH of the resultant solution.

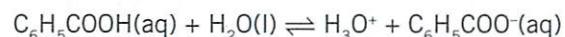
Solution: The species initially present are the weak acid, C_6H_5COOH , and the strong base, $NaOH$. These will react.

First, write the equation for the reaction. The strong base is the limiting reagent and, because it is strong, it is simply written as OH^- .



Initial:	0.0500	0.0200	0
After:	0.0300	0	0.0200

When the reaction is complete, both the weak acid, C_6H_5COOH , and the conjugate base, $C_6H_5COO^-$, are present in roughly equal amounts. Once the buffer solution is formed, it is treated as an equilibrium containing a common ion. A buffer solution may be calculated using moles for the parent and conjugate species.



Equilibrium: 0.0300 moles x 0.0200 moles

$$K_a = 6.3 \times 10^{-5} = \frac{[H_3O][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{(x)(0.0200)}{(0.0300)}$$

Solving: $x = 9.45 \times 10^{-5} M = [H_3O^+]$ and $pH = 4.02$

The same principles can be applied to the reaction of excess weak base with a strong acid; this reaction will also result in the formation of a buffer solution.

Example 3.4.6. pH of an Ammonium Buffer (In-Class Exercise)

250 mL of 0.135 M ammonia (NH_3) are mixed with 150 mL of 0.110 M HNO_3 . Calculate the pH of this solution.

Data: K_b for $NH_3 = 1.8 \times 10^{-5}$



HOW BUFFERS WORK

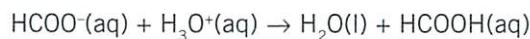
Buffer solutions resist changes in pH. If a small amount of strong acid is added to an acid buffer, it will react with the conjugate base component of the buffer to produce more of the weak acid. The ratio of these two components will change only slightly, which results in a small drop in pH. A similar reaction will take place if a small amount of strong base is added to the same buffer. The weak acid will react with the strong base, producing more conjugate base. Once again, the ratio of weak acid to conjugate base does not change very much. In this case, the pH of the solution will increase.

Example 3.4.7. Adding Strong Acid to a Buffer

A buffer solution consists of 0.200 moles of formic acid, HCOOH, and 0.150 moles of sodium formate, HCOONa, in 2.0 L of solution. The pH of the initial buffer solution is 3.60. What is the effect on the pH if 0.0300 moles of HCl are added to the buffer solution?

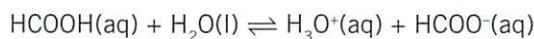
Data: K_a for HCOOH = 1.9×10^{-4}

Solution: This buffer solution consists of a weak acid, HCOOH, and its conjugate base, HCOO⁻ (which comes from HCOONa). HCl is a strong acid and it will react with the conjugate base to form more of the weak acid. The quantities used in the following reaction are moles:



Initial:	0.150	0.0300	0.200
After:	0.150 – 0.0300	0	0.200 + 0.0300
	= 0.120		0.230

Examination of the species present after the reaction shows both the weak acid and its conjugate base are still present. Only their quantities have changed a little. This solution is still a buffer so the moles of the acid and its conjugate base, after the reaction, can be used. It is not necessary to calculate the molarity of those species.



Initial:	0.230	0	0.120
Equilibrium:	0.230 – x	x	0.120 + x

Note that subtracting or adding concentration values from/to mole amounts would be unworkable if not for the fact that the value of x were negligible.

Since x is negligible:

$$K_a = 1.9 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(x)(0.120)}{(0.230)}$$

Solving: $x = 3.64 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$ and $\text{pH} = 3.44$

The pH of the solution decreased by 0.16 pH units after adding the strong acid.

Examine the ratio of conjugate base to weak acid before and after the addition of the HCl:

$$\text{Before the HCl: } \frac{\text{HCOO}^-}{\text{HCOOH}} = \frac{0.150 \text{ mol}}{0.200 \text{ mol}} = 0.75$$

$$\text{After the HCl: } \frac{\text{HCOO}^-}{\text{HCOOH}} = \frac{0.120 \text{ mol}}{0.230 \text{ mol}} = 0.52$$

The small change in the ratio results in a small change in pH.

Example 3.4.8. Adding Strong Base to a Buffer (In-Class Exercise)

The buffer solution in the previous example consists of 0.200 moles of HCOOH and 0.150 moles of HCOONa in 2.0 L of solution. Calculate the change in pH if 1.60 g of NaOH are added to the solution.

Data: K_a for HCOOH = 1.9×10^{-4}

Comparing a Buffer Solution to Water

The previous examples have shown how adding a small amount of a strong acid or base to a buffer solution results in a small change in pH. What happens when (a) 0.0300 moles of HCl or (b) 1.60 g of NaOH are added to 2.00 L of water?

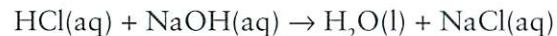
- When 0.0300 moles of HCl are added to 2.00 L of water ($\text{pH} = 7.0$), the $[\text{H}_3\text{O}^+] = 0.0150 \text{ M}$. The pH of the solution is 1.82 (i.e., it decreases by 5.18 pH units). The same amount of HCl causes the pH of the buffer solution to decrease by only 0.17 pH units.

- b. When 1.60 g of NaOH (0.0400 moles) are added to 2.00 L of water ($\text{pH} = 7.0$), the $[\text{OH}^-] = 0.0200\text{ M}$. The pH of this solution is 12.3 (i.e., increases by 5.3 pH units). Compare this increase to the small increase observed when the same amount of NaOH is added to a buffer solution.

ACID–BASE TITRATIONS

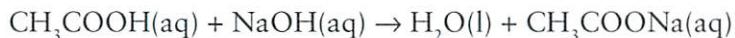
Acid–base titration is a method used to determine parameters such as the concentration of base (or acid) in a solution. There are two possibilities in a titration process: acid is added to neutralize a base, or a base is added to neutralize an acid. The *equivalence point* of a titration is reached when stoichiometrically equivalent amounts of acid and base have been combined. For example, the equivalence point is reached when mixing 0.1 mol HCl with 0.1 mol of NaOH; or 0.2 mol CH_3COOH with 0.1 mol $\text{Ca}(\text{OH})_2$. The pH at the equivalence point is not always 7.0, as shown in the examples below.

Case 1: Strong acid–strong base:



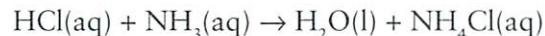
At the equivalence point, all of the HCl and NaOH have reacted with each other, resulting in a solution of NaCl. Since both Na^+ and Cl^- are spectator ions, the solution is neutral (pH 7).

Case 2: Weak acid–strong base:



At the equivalence point, all of the CH_3COOH and NaOH have reacted with each other, resulting in a solution of CH_3COONa . Na^+ is a spectator ion and the acetate (CH_3COO^-) is a weak base, so the solution is basic.

Case 3: Strong acid–weak base:



At the equivalence point, all of the HCl and NH_3 have reacted, resulting in a solution of NH_4Cl . Cl^- is a spectator ion and the ammonium ion (NH_4^+) is a weak acid, so the solution is acidic.

The products of the ionization reaction of the salt determines whether the final solution is acidic or basic. Note that any reaction involving a strong species will go to completion and therefore, a unidirectional arrow (\rightarrow) is used.

pH at Equivalence Point

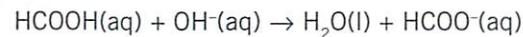
It is often useful to determine the pH at the equivalence point of a titration. As seen in the acid–base titration lab, a colour change of an indicator signals the arrival at the equivalence point if an appropriate indicator was used. Because different indicators change colours at different pHs, having an estimate of the equivalence point pH enables a chemist to select the appropriate indicator.

For any titration involving a weak species and a strong species (such as formic acid and NaOH, respectively), an equilibrium will be established between the excess weak species and the just-formed conjugate species. This is, of course, a buffer solution. At the equivalence point, the only species present is the conjugate, which will then react with water. It is this reaction of the conjugate species that is ultimately responsible for the pH of the solution at the equivalence point. Thus, when determining the pH at the equivalence point, the acid–base reaction must be used to accurately determine the amount of conjugate formed.

Example 3.4.9. pH at the Equivalence Point of a Weak Acid–Strong Base Titration

Find the pH at the equivalence point of the titration of 25.00 mL of 0.165 M formic acid, HCOOH ($K_a = 1.9 \times 10^{-4}$), with 0.185 M KOH.

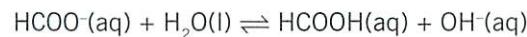
Solution: First, write the reaction between the acid and base, assuming the reaction goes to completion:



At the equivalence point of this titration, the number of moles of weak acid will be equal to the number of moles of strong base:

$$\# \text{ moles HCOOH} = 0.165 \text{ M} \times 0.02500 \text{ L} = 0.004125 \text{ moles} = \text{moles OH}^-$$

From the stoichiometry of the reaction, the number of moles of HCOO^- produced must be equal to the number of moles of HCOOH initially (0.004125 moles). To calculate the pH, the hydrolysis reaction of HCOO^- with water must be considered:



Initial:	c	0	0
Equilibrium:	$c - x$	x	x

c is the initial $[\text{HCOO}^-]$. This can be calculated from the number of moles of HCOO^- produced in the reaction and the total volume of the solution. To determine the total volume of the solution, the volume of the strong base used must first be calculated.

$$\text{Volume OH}^- = \text{Volume KOH} = \frac{0.004125 \text{ moles}}{0.185 \text{ M}} = 0.02230 \text{ L}$$

$$[\text{HCOO}^-] = \frac{0.004125 \text{ moles}}{(0.02500 + 0.02230) \text{ L}} = 0.08721 \text{ M} = c$$

The equilibrium constant expression is: $K_b = \frac{x^2}{c - x}$

In order to solve for x in this expression, K_b for HCOO^- must be calculated using K_a for HCOOH and K_w .

$$K_b = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.26 \times 10^{-11}; \text{ substituting: } 5.26 \times 10^{-11} = \frac{x^2}{0.08721 - x}$$

A comparison of c and K_b indicates that using the approximation $0.08721 - x \approx 0.08721$ is valid.

$$\text{Therefore: } x = \sqrt{0.08721 \times 5.26 \times 10^{-11}} = 2.142 \times 10^{-6} = [\text{OH}^-]$$

To find pH, pOH must first be calculated using $[\text{OH}^-]$:

$$\text{pOH} = 5.67, \text{ so pH} = 14 - 5.67 = 8.33$$

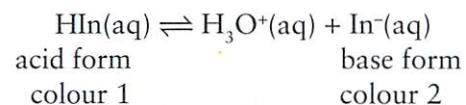
Example 3.4.10. pH at the Equivalence Point of a Weak Base–Strong Acid Titration (In-Class Exercise)

Calculate the equivalence point pH for the titration of 0.175 M methylamine (CH_3NH_2) with 0.250 M HNO_3 .

Data: K_b for $\text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}$

Acid–Base Indicators

Acid–base indicators are used to detect the equivalence point in a titration. An indicator is a weak organic acid (represented by HIn) that has a different colour than its conjugate base. As a weak acid, it will set up the following equilibrium:



In an acidic solution, the indicator mostly exists in its acid form (colour 1). Conversely, under basic conditions it mostly exists in its base form (colour 2). The colour change takes place around the pH value where $[\text{HIn}] = [\text{In}^-]$. The equilibrium constant expression for the indicator is:

$$K_{\text{HIn}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

When $[\text{HIn}] = [\text{In}^-]$, then $K_{\text{HIn}} = [\text{H}_3\text{O}^+]$ which gives $\text{p}K_{\text{HIn}} = \text{pH}$. Therefore, the $\text{p}K_{\text{HIn}}$ of the indicator is equal to the pH at which the colour change occurs.

- At 1 pH unit below this pH or $\text{p}K_a$ value (acidic) the indicator is about 90% in the HIn form.
- At 1 pH unit above this pH or $\text{p}K_a$ value (basic) the indicator is about 90% in the In^- form.
- The point of the titration at which the indicator changes colour is called the endpoint.

Note that the indicator is present in a very low concentration. The value of $[\text{H}_3\text{O}^+]$, and hence the pH, is driven by the acid–base reaction and is NOT affected by the presence of the indicator.

When an indicator is being chosen for a titration, it is important that it changes colour at (or close to) the pH of the equivalence point. Therefore, the ability to predict the pH at the equivalence point (as shown in previous examples) enables one to choose the correct indicator. For the reasons described above, it is best to choose an indicator that has a $\text{p}K_a$ value within one unit of the pH of the solution at the equivalence point.



Different types of titrations will have different equivalence-point pH values. For a strong acid–strong base titration, the pH at the equivalence point will be 7. In theory, an indicator chosen for this type of titration should have a pK_a between 5 and 9. In practice, however, almost any indicator may be used because the pH change is very large near the equivalence point.

More care must be used when choosing an indicator for titrations that involve a weak species. For a weak acid–strong base titration, the pH at the equivalence point will be above 7, usually in the range of pH 8 to pH 10. The indicator chosen must have a pK_a in this range. An example of this type of indicator is phenolphthalein, which has a pK_a of about 9.

The choice of indicator is also critical for weak base–strong acid titrations. In these titrations, the pH at the equivalence point will be below 7, usually in the range of pH 4 to pH 6. An example of a suitable indicator for this titration is methyl red, with a pK_a of about 5.

Table 3.4.1 shows some typical indicators, their pK_a values and applicable titrations.

TABLE 3.4.1 TYPICAL pK_a INDICATOR VALUES

TITRATION	EQUIVALENCE POINT pH	DESIRED INDICATOR pK_a	TYPICAL INDICATOR
Strong acid–strong base	neutral	around 7*	bromothymol blue
Strong acid–weak base	acidic	4–6	methyl red
Weak acid–strong base	basic	8–10	phenolphthalein

* In practice, almost any indicator may be used for this type of titration because the pH change at equivalence is extremely large.

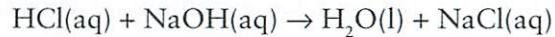
TITRATION CURVES

In the previous topic, the equivalence point of a titration was introduced. In the case of either a weak acid–strong base or a weak base–strong acid titration, the only species present at the equivalence point (in addition to water and the spectator ions) is the conjugate species of the original weak acid or base. The conjugate species then undergoes a hydrolysis reaction with the water. It is this reaction that accounts for the fact that the pH at the equivalence point of a titration is not always 7.

There are other processes occurring both before and after the equivalence point in a titration, and those processes depend on the type of titration. A titration curve shows, in the form of a graph, the pH resulting from all the reactions occurring during a titration (see Figure 3.4.5).

Strong Acid–Strong Base Titration

An example of this type of titration is:



The titration curve plots the pH of the solution versus the volume of base added to the acid. At the beginning of the titration, the solution is strongly acidic due to the presence of excess or unreacted HCl. Even though NaOH is being added, the reaction between the HCl and the NaOH occurs virtually instantaneously, leaving slightly less HCl in solution. Keep in mind that the pH scale is logarithmic. Reacting 90% of the available acid will only increase the pH by one unit.

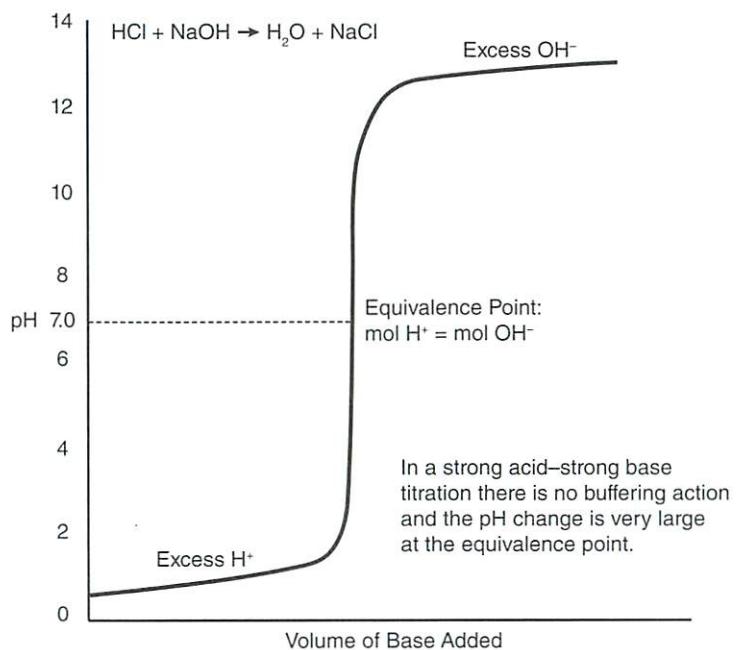


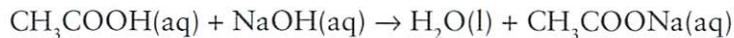
Figure 3.4.5 Titration curve for a strong acid–strong base.

As the equivalence point is approached, there is very little HCl left in the solution so the pH begins to increase, culminating in a very rapid increase just before and after the equivalence point. The equivalence point occurs at the inflection point of the curve.

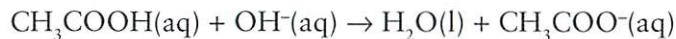
At the equivalence point, the pH is 7 and the only species present in the solution are NaCl and water. If more NaOH is added after the equivalence point has been reached, a basic solution results. Just past the equivalence point, the pH will continue to increase rapidly. Once a basic solution is achieved, the pH will appear to almost level off, increasing only very slightly.

Weak Acid–Strong Base Titration

A typical example of this type of titration is:



As the base is strong and therefore completely ionized, it is shown as OH^- for increased clarity:



At the beginning of this titration, the solution is acidic due to the presence of CH_3COOH . As this is a weak acid, the pH will be higher than it would be in the case of a strong acid with the same concentration. Once the addition of OH^- begins, the conjugate base, CH_3COO^- will be formed. In the early stages of the titration, there will still be weak acid present, so the presence of both the weak acid and its conjugate base produces a buffer solution.

The pH will continue to increase (see Figure 3.4.6), but only gradually as the OH^- is added. This is another illustration of the ability of a buffer solution to resist large changes in pH. At the midpoint of the titration (half of the volume needed to reach the equivalence point), the pH of the solution equals the $\text{p}K_a$ of the acid due to the 1:1 ratio of the acid and conjugate:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

At the midpoint, $[\text{A}^-] = [\text{HA}]$

$$\therefore K_a = [\text{H}^+]$$

and

$$\text{p}K_a = \text{pH}$$

As the equivalence point is reached, there is so little weak acid left that the buffering capability of the solution is diminished. The pH will increase rapidly just before the equivalence point and continue the sharp increase after the equivalence point. Once again, the equivalence point is at the inflection point of the curve.

At the equivalence point, the only species present that may react are the conjugate base and water. The reaction of the conjugate base produces a basic solution. At the equivalence point of a weak acid–strong base titration, the solution is basic.

After the equivalence point, the pH will increase until the solution is strongly basic due to an excess of $\text{OH}^-(\text{aq})$. The pH will continue to increase only slightly as the excess amount of $\text{OH}^-(\text{aq})$ increases.

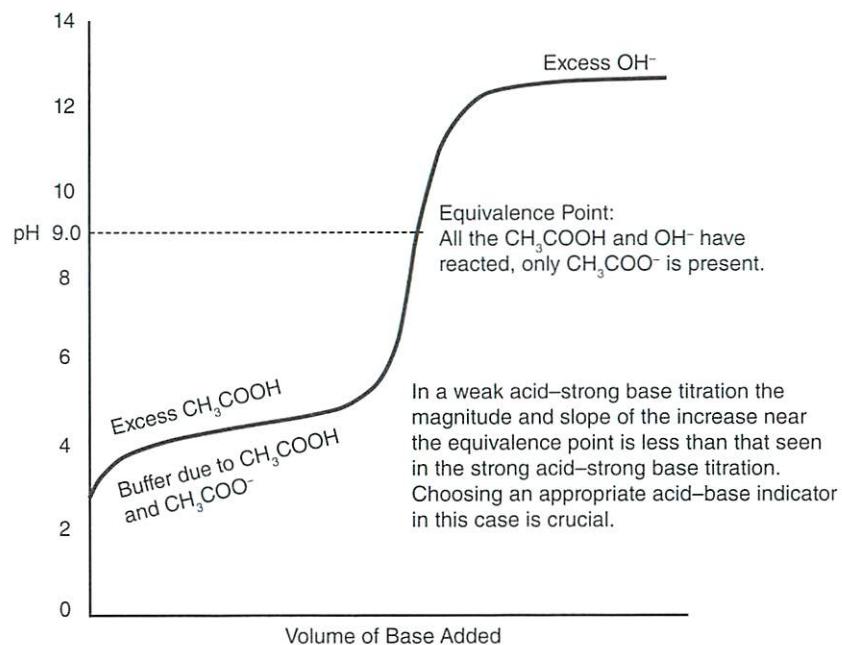
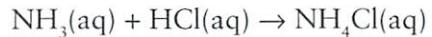


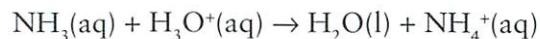
Figure 3.4.6 Titration curve for a weak acid–strong base.

Weak Base–Strong Acid Titration

Another familiar example helps illustrate a weak base–strong acid titration:



Because the acid is strong, it is shown as H_3O^+ , the result of the complete ionization of HCl:



In this titration, the initial pH will be basic due to the presence of the weak base. As the strong acid is added, the reaction shown above occurs, producing the conjugate acid (NH_4^+). Both the weak base and its conjugate acid are present. This region of the titration curve represents the “buffered” solution (see Figure 3.4.7).

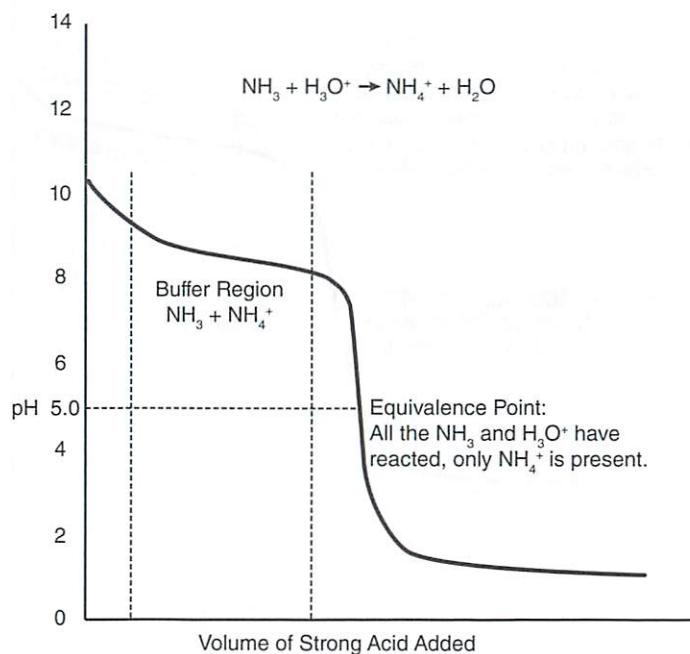


Figure 3.4.7 Titration curve for a weak base–strong acid.

As more of the strong acid is added, most and then all of the weak base will be consumed and the solution will no longer be a buffer.

At the midpoint of this titration, the pH of the solution = pK_b of the base:

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

At the midpoint, $[\text{HB}^+] = [\text{B}]$

$$\therefore K_b = [\text{OH}^-]$$

and

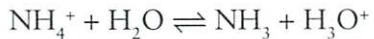
$$pK_b = p\text{OH}$$

or

$$\text{pH} = 14 - pK_b$$

When the number of moles of HCl added is equal to the initial moles of NH_3 , the solution is at the equivalence point and contains only the salt NH_4Cl (ammonium chloride). The pH is < 7.0 as the solution contains the ammonium ion, the conjugate acid of ammonia. When adding strong acid to weak conjugate acid, the pH will fall rapidly.

Consider what effect the presence of the strong acid HCl has on the percent hydrolysis of the weak acid NH_4^+ . Note that the ammonium ion would normally undergo hydrolysis according to:



The strong acid, HCl, is fully ionized in solution, and if 0.10 moles of HCl are added beyond the equivalence point, there will be 0.10 moles of H_3O^+ present in the solution. The H_3O^+ suppresses the ionization of ammonium.

Example 3.4.11. Weak Base–Strong Acid Titration (In-Class Exercise)

Referring to the titration curve shown in Figure 3.4.7, suppose that 25.0 mL of 0.400 M NH_3 is titrated with 0.200 M HCl.

1. Determine the pH:
 - a. After 20.0 mL of HCl are added.
 - b. At the equivalence point.
 - c. If 65.0 mL of HCl are added.
2. Find the percent ionization of the NH_4^+ at points (b) and (c).

Section 3.4 Review Problems

1. Determine whether the following combinations of species will produce a buffer solution.
 - a. 250 mL of 0.150 M HNO_2 and 100 mL of 0.150 M NaOH
 - b. 7.20 g of $\text{C}_6\text{H}_5\text{COONa}$ and 500 mL of 0.100 M HClO_4
 - c. 500 mL of 0.250 M $(\text{CH}_3)_2\text{NH}$ and 525 mL of 0.100 M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$
 - d. 300 mL of 0.125 M $\text{CH}_3\text{NH}_3\text{Cl}$ and 125 mL of 0.100 M KOH
 - e. 400 mL of 0.115 M NH_4NO_3 and 200 mL of 0.110 M HNO_3
2. Supply the missing words to complete the following three sentences:
 - a. A buffer solution contains two components, either a _____ acid and its _____, or a _____ base and its _____.
 - b. The pH of a buffer depends only on the _____ of the concentrations of the two components, so it is _____ by dilution.
 - c. If strong acid is added to a buffer mixture, it is removed by reaction with the _____ component, while added strong base is removed by reaction with the _____ component.
3. A solution is made from 0.200 mol formic acid, HCOOH , and 0.500 mol potassium formate, HCOOK , diluted to 750 mL volume. Formic acid has $K_a = 1.9 \times 10^{-4}$. Calculate:
 - a. The pH of this solution.
 - b. The change in pH if the total volume is diluted to 2.00 L with water.
 - c. The change in pH if 4.0 g of sodium hydroxide is added.
4. What mass, in grams, of NaNO_2 must be added to 700 mL of 0.165 M HNO_2 to produce a solution with a pH of 3.50?

Data: K_a for $\text{HNO}_2 = 4.5 \times 10^{-4}$

5. Answer the following:

- Calculate the pH of aqueous ammonia, concentration 0.12 M ($K_b = 1.8 \times 10^{-5}$).
- 4.40 g of ammonium chloride, NH_4Cl , is added to a 500 mL portion of 0.12 M aqueous ammonia. What is the change in pH?
- How will the pH of the solution in (b) change if the solution is diluted to 1.0 L volume?
- How will the pH of the solution in (b) change if 50 mL of 1.0 M HCl is added?

6. Answer the following:

- What mass of sodium acetate should be dissolved in 1.00 L of acetic acid, 0.150 M concentration, in order to produce a buffer with pH = 4.5? (K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$)
- What mass of NH_4NO_3 must be added to 500 ml of 0.85 M $\text{NH}_3\text{(aq)}$ in order to prepare a buffer solution with a pH of 9.70? (K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$)

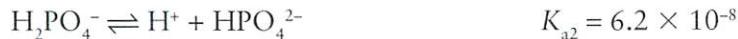
7. Answer the following:

- What mass of sodium acetate must be added to 500 mL of 1.00 M acetic acid to provide a solution of pH = 5.00? (K_a for acetic acid is 1.8×10^{-5})
- What is the effect on the pH of the above solution of adding: (i) 50 mL of 1.00 M HCl(aq) (ii) 50 mL of 1.00 M NaOH(aq)?

8. Answer the following:

- In contrast to hydrides of the other halogens, HF is a weak acid, with $K_a = 7.2 \times 10^{-4}$. What would be the pH of a solution made by adding 1.00 g of solid NaOH to 50.0 mL of 1.00 M HF?
- 50 mL of a 1.00 M solution of HF is titrated with 1.00 M KOH solution. What would the pH be when 25 mL of the KOH solution has been added?
- Suppose 25 mL of 1.00 M HCl is added to 50 mL of 1.00 M HF. What is the pH and the percent ionization of the HF in this solution?

9. Phosphate buffers are important in controlling the pH of physiological fluids, including blood. An important equilibrium is that for the second dissociation of phosphoric acid (H_3PO_4):



If blood has a pH of 7.40, what is the ratio $[\text{H}_2\text{PO}_4^-] / [\text{HPO}_4^{2-}]$?

10. Carbonic acid, H_2CO_3 , has $K_{a1} = 4.4 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$. Calculate the pH of:

- 0.20 mol sodium carbonate, Na_2CO_3 , and 0.40 mol sodium hydrogen carbonate, NaHCO_3 , in solution in a 500 mL volume.
- 0.050 mol sodium hydrogen carbonate, NaHCO_3 , and 0.010 mol of carbonic acid, H_2CO_3 , in solution in a 100 mL volume.

11. When 35.0 mL of 0.200 M acetic acid ($K_a = 1.8 \times 10^{-5}$) is titrated with 0.250 M NaOH solution, what is the pH at the equivalence point?

12. Calculate the pH in the following solutions.

- At the equivalence point when 0.500 M nitrous acid (HNO_2) is titrated with 0.100 M NaOH.
- At the equivalence point when 0.800 M methylamine (CH_3NH_2) is titrated with 0.400 M HCl.

13. Joe Student is titrating two weak acids with KOH solution. They have the same original concentration, but acid A is 10% dissociated while acid B is stronger and is 20% dissociated. Joe therefore expects acid B to require twice the volume of KOH solution that acid A requires. However, it doesn't work out that way. What is wrong with Joe's reasoning?

14. Three indicators are available: bromocresol purple, $\text{p}K_a = 6.8$; bromophenol blue, $\text{p}K_a = 3.9$; *o*-cresolphthalein, $\text{p}K_a = 8.9$. Without performing detailed pH calculations, which indicator should be used for each of the following titrations:

- $\text{NH}_3(\text{aq})$ with HNO_3
- $\text{Ba}(\text{OH})_2$ with HBr
- LiOH with HCOOH

