

LECTURE – 4

2.4.2 Acid–Base Reactions

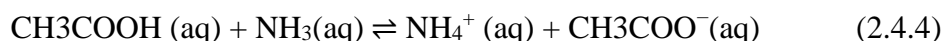
2.4.3 Complexation Reactions

2.4.4 Oxidation–Reduction (Redox) Reactions

2.4.2 Acid–Base Reactions

A useful definition of acids and bases is that independently introduced in 1923 by Johannes Brønsted and Thomas Lowry. In the Brønsted-Lowry definition, an **acid** is a proton donor and a **base** is a proton acceptor.

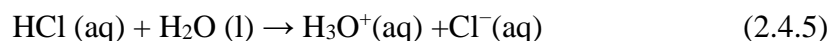
Note : the connection in these definitions—defining a base as a proton acceptor implies that there is an acid available to donate the proton. For example, in reaction 2.4.4 acetic acid, CH₃COOH, donates a proton to ammonia, NH₃, which serves as the base.



When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, CH₃COO⁻, in reaction 2.4.4 is a base that can accept a proton from the acidic ammonium ion, NH₄⁺, forming acetic acid and ammonia. We call the acetate ion the conjugate base of acetic acid, and the ammonium ion is the conjugate acid of ammonia.

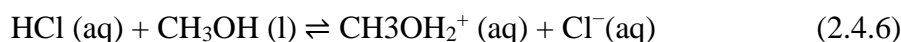
Strong and Weak Acids

The reaction of an acid with its solvent (typically water) is an acid dissociation reaction. We divide acids into two categories—strong and weak—based on their ability to donate a proton to the solvent. A strong acid, such as HCl, almost completely transfers its proton to the solvent, which acts as the base.

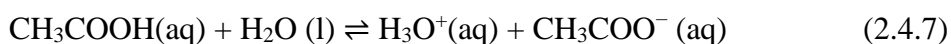


We use a single arrow (→) in place of the equilibrium arrow (⇌) because we treat HCl as if it completely dissociates in aqueous solutions. In water, the common strong acids are hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), nitric acid (HNO₃), perchloric acid (HClO₄), and the first proton of sulfuric acid (H₂SO₄).

Note : In a different solvent, HCl may not be a strong acid. For example, HCl does not act as a strong acid in methanol. In this case we use the equilibrium arrow when writing the acid–base reaction.



A weak acid, of which aqueous acetic acid is one example, does not completely donate its acidic proton to the solvent. Instead, most of the acid remains undissociated, with only a small fraction present as the conjugate base.



The equilibrium constant for this reaction is an **acid dissociation constant**, K_a , which we write as

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}$$

2.4.8

Note

Earlier we noted that we omit pure solids and pure liquids from equilibrium constant expressions. Because the solvent, H₂O, is not pure, you might wonder why we have not included it in acetic acid's K_a expression. Recall that we divide each term in the equilibrium constant expression by its standard state value. Because the concentration of H₂O is so large—it is approximately 55.5 mol/L—its concentration as a pure liquid and as a solvent are virtually identical. The ratio

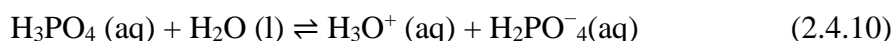
$$\frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]^\circ}$$

6.4.9

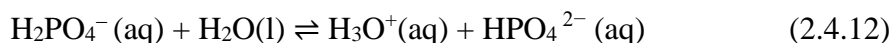
is essentially 1.00.

The magnitude of K_a provides information about a weak acid's relative strength, with a smaller K_a corresponding to a weaker acid. The ammonium ion, NH₄⁺, for example, with a K_a of 5.702 × 10⁻¹⁰, is a weaker acid than acetic acid.

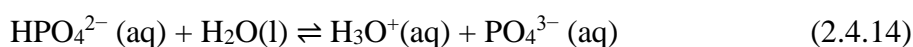
Monoprotic weak acids, such as acetic acid, have only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have more than one acidic proton, each characterized by an acid dissociation constant. We call such acids **polyprotic** weak acids. Phosphoric acid, for example, has three acid dissociation reactions and three acid dissociation constants.



$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3} \quad (2.4.11)$$



$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8} \quad (2.4.13)$$

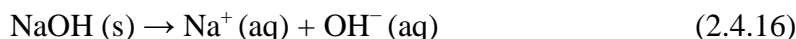


$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13} \quad (2.4.15)$$

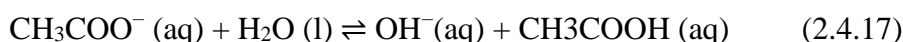
The decrease in the acid dissociation constants from K_{a1} to K_{a3} tells us that each successive proton is harder to remove. Consequently, H_3PO_4 is a stronger acid than $H_2PO_4^-$, and $H_2PO_4^-$ is a stronger acid than HPO_4^{2-} .

Strong and Weak Bases

The most common example of a strong base is an alkali metal hydroxide, such as sodium hydroxide, NaOH, which completely dissociates to produce hydroxide ion.



A weak base, such as the acetate ion, CH_3COO^- , only partially accepts a proton from the solvent, and is characterized by a **base dissociation constant**, K_b . For example, the base dissociation reaction and the base dissociation constant for the acetate ion are

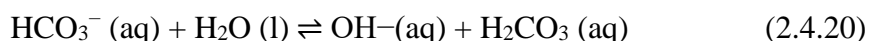
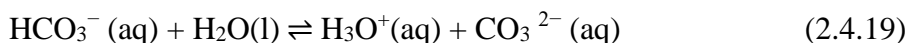


$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.7 \times 10^{-10} \quad (2.4.18)$$

A polyprotic weak base, like a polyprotic acid, has more than one base dissociation reaction and more than one base dissociation constant.

Amphiprotic Species

Some species can behave as either a weak acid or as a weak base. For example, the following two reactions show the chemical reactivity of the bicarbonate ion, HCO_3^- , in water.



A species that is both a proton donor and a proton acceptor is called **amphiprotic**. Whether an amphiprotic species behaves as an acid or as a base depends on the equilibrium constants for the competing reactions. For bicarbonate, the acid dissociation constant for reaction 2.4.19

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad (2.4.21)$$

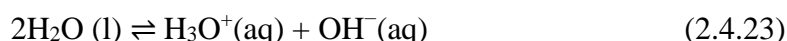
is smaller than the base dissociation constant for reaction 2.4.20.

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.25 \times 10^{-8} \quad (2.4.22)$$

Because bicarbonate is a stronger base than it is an acid, we expect an aqueous solution of HCO_3^- to be basic.

Dissociation of Water

Water is an amphiprotic solvent because it can serve as an acid or as a base. An interesting feature of an amphiprotic solvent is that it is capable of reacting with itself in an acid–base reaction.



We identify the equilibrium constant for this reaction as water's dissociation constant, K_w ,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (2.4.24)$$

which has a value of 1.0000×10^{-14} at a temperature of 24°C . The value of K_w varies substantially with temperature. For example, at 20°C K_w is 6.809×10^{-15} , while at 30°C K_w is 1.469×10^{-14} . At 25°C , K_w is 1.008×10^{-14} , which is sufficiently close to 1.00×10^{-14} that we can use the latter value with negligible error.

An important consequence of equation 6.4.24 is that the concentration of H_3O^+ and the concentration of OH^- are related. If we know $[\text{H}_3\text{O}^+]$ for a solution, then we can calculate $[\text{OH}^-]$ using Equation 6.4.24 .

Example 2.3

What is the $[\text{OH}^-]$ if the $[\text{H}_3\text{O}^+]$ is $6.12 \times 10^{-5} \text{ M}$?

Solution

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{6.12 \times 10^{-5}} = 1.63 \times 10^{-10} \quad (2.4.25)$$

The pH Scale

Equation 6.4.24 allows us to develop a **pH scale** that indicates a solution's acidity ($\text{pH} = -\log[\text{H}_3\text{O}^+]$). When the concentrations of H_3O^+ and OH^- are equal a solution is neither acidic nor basic; that is, the solution is neutral. Letting

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] \quad (2.4.26)$$

substituting into equation 2.4.24

$$K_w = [\text{H}_3\text{O}^+]^2 = 1.00 \times 10^{-14} \quad (2.4.27)$$

and solving for $[H_3O^+]$ gives

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \quad (2.4.28)$$

A neutral solution **at room temperature** has a hydronium ion concentration of 1.00×10^{-7} M and a pH of 7.00. For a solution to be acidic the concentration of H_3O^+ must be greater than that for OH^- , which means that

$$[H_3O^+] > 1.00 \times 10^{-7} \text{ M} \quad (2.4.29)$$

The pH of an acidic solution, therefore, must be less than 7.00. A basic solution, on the other hand, has a pH greater than 7.00. Figure 6.2 shows the pH scale and pH values for some representative solutions.

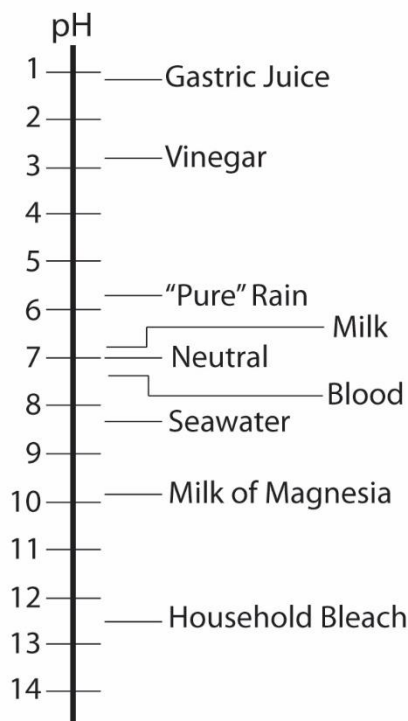
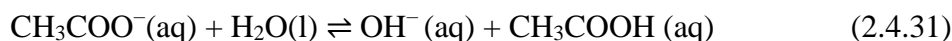
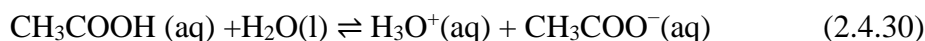


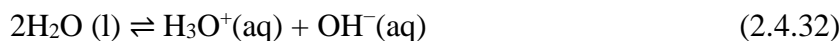
Figure 2.2: Scale showing the pH value for representative solutions. Milk of Magnesia is a saturated solution of $Mg(OH)_2$.

Tabulating Values for K_a and K_b

A useful observation about acids and bases is that the strength of a base is inversely proportional to the strength of its conjugate acid. Consider, for example, the dissociation reactions of acetic acid and acetate.



Adding together these two reactions gives the reaction



for which the equilibrium constant is K_w . Because adding together two reactions is equivalent to multiplying their respective equilibrium constants, we may express K_w as the product of K_a for CH_3COOH and K_b for CH_3COO^- .

$$K_w = K_{a,\text{CH}_3\text{COOH}} \times K_{b,\text{CH}_3\text{COO}^-} \quad (2.4.33)$$

For any weak acid, HA, and its conjugate weak base, A^- , we can generalize this to the following equation.

$$K_w = K_{a,\text{HA}} \times K_{b,\text{A}^-} \quad (2.4.34)$$

The relationship between K_a and K_b for a conjugate acid–base pair simplifies our tabulation of acid and base dissociation constants. Appendix 11 includes acid dissociation constants for a variety of weak acids. To find the value of K_b for a weak base, use equation 6.4.34 and the K_a value for its corresponding weak acid.

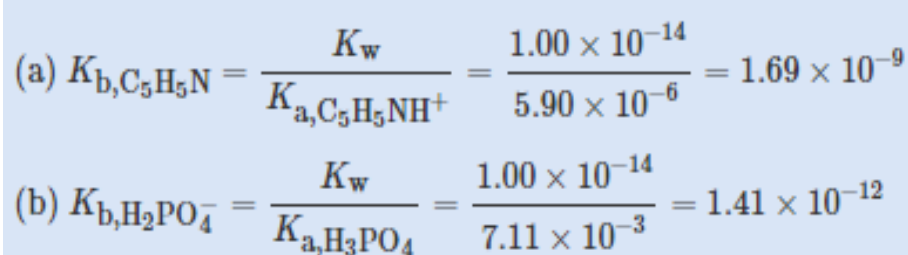
Note : A common mistake when using equation 2.4.34 is to forget that it applies only to a conjugate acid–base pair.

Example 2.4

Using [Appendix 11](#), calculate values for the following equilibrium constants.

- (a) K_b for pyridine, $\text{C}_5\text{H}_5\text{N}$
- (b) K_b for dihydrogen phosphate, H_2PO_4^-

Solution


$$\begin{aligned} \text{(a)} \quad K_{b,\text{C}_5\text{H}_5\text{N}} &= \frac{K_w}{K_{a,\text{C}_5\text{H}_5\text{NH}^+}} = \frac{1.00 \times 10^{-14}}{5.90 \times 10^{-6}} = 1.69 \times 10^{-9} \\ \text{(b)} \quad K_{b,\text{H}_2\text{PO}_4^-} &= \frac{K_w}{K_{a,\text{H}_3\text{PO}_4}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12} \end{aligned}$$

When finding the K_b value for polyprotic weak base, you must be careful to choose the correct K_a value. Remember that equation 2.4.34 applies only to a conjugate acid–base pair. The conjugate acid of H_2PO_4^- is H_3PO_4 , not HPO_4^{2-} .

Practice Exercise 2.2 Using [Appendix 11](#), calculate the K_b values for hydrogen oxalate, HC_2O_4^- , and oxalate $\text{C}_2\text{O}_4^{2-}$. The K_b for hydrogen oxalate is

$$K_{b,HC_2O_4^-} = \frac{K_w}{K_{a,H_2C_2O_4}} = \frac{1.00 \times 10^{-14}}{5.60 \times 10^{-2}} = 1.79 \times 10^{-13}$$

and the K_b for oxalate is

$$K_{b,C_2O_4^{2-}} = \frac{K_w}{K_{a,HC_2O_4^-}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.85 \times 10^{-10}$$

As we expect, the K_b value for $C_2O_4^{2-}$ is larger than that for $HC_2O_4^-$.

Why $[H_2O]$ Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions

In a dilute aqueous solution, the molar concentration of water is

$$[H_2O] = \frac{1000. \text{g-H}_2\text{O}}{\text{L H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.0. \text{g-H}_2\text{O}} = 55.6 \text{ M}$$

Suppose we have 0.1 mol of HCl in 1 L of water. The presence of this acid will shift the equilibrium shown in Equation 9-9 to the left. Originally, however, there were only 10^{-7} mol/L OH^- to consume the added protons. Thus, even if all the OH^- ions are converted to H_2O , the water concentration will increase to only

$$[H_2O] = 55.6 \frac{\text{mol H}_2\text{O}}{\text{L H}_2\text{O}} + 1 \times 10^{-7} \frac{\text{mol-OH}^-}{\text{L H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{\text{mol-OH}^-} \approx 55.6 \text{ M}$$

The percent change in water concentration is

$$\frac{10^{-7} \text{ M}}{55.6 \text{ M}} \times 100\% = 2 \times 10^{-7}\%$$

which is certainly inconsequential. Thus, $K[H_2O]^2$ in Equation 9-10 is, for all practical purposes, a constant. That is,

$$K(55.6)^2 = K_w = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$



$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad (9-10)$$

$$K(55.6)^2 = K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (9-11)$$

At 25°C, the ion-product constant for water is 1.008×10^{-14} . For convenience, we use the approximation that at room temperature $K_w \approx 1.00 \times 10^{-14}$. Table 9-3 shows the dependence of this constant on temperature. The ion-product constant for water permits the ready calculation of the hydronium and hydroxide ion concentrations of aqueous solutions.

TABLE 9-3

Variation of K_w with Temperature

Temperature, °C	K_w
0	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
100	49×10^{-14}

Example 2.5

Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C.

Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Substitution into Equation 9-11 gives

$$[\text{H}_3\text{O}^+]^2 = [\text{OH}^-]^2 = K_w$$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w}$$

(continued)

At 25°C,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$

At 100°C, from Table 9-3,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7} \text{ M}$$

Example 2.6

Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C.

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. As in Example 9-1, hydroxide ions and hydronium ions are formed *in equal amounts* from dissociation of water. Therefore, we write

$$[\text{OH}^-] = 0.200 + [\text{H}_3\text{O}^+]$$

where $[\text{H}_3\text{O}^+]$ accounts for the hydroxide ions contributed by the solvent. The concentration of OH^- from the water is insignificant, however, when compared with 0.200, so we can write

$$\begin{aligned}[\text{OH}^-] &\approx 0.200 \\ \text{pOH} &= -\log 0.200 = 0.699\end{aligned}$$

Equation 9-11 is then used to calculate the hydronium ion concentration:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14} \text{ M} \\ \text{pH} &= -\log 5.00 \times 10^{-14} = 13.301\end{aligned}$$

Note that the approximation

$$[\text{OH}^-] = 0.200 + 5.00 \times 10^{-14} \approx 0.200 \text{ M}$$

causes no significant error.

2.4.3 Complexation Reactions

A more general definition of acids and bases was proposed in 1923 by G. N. Lewis. The Brønsted-Lowry definition of acids and bases focuses on an acid's proton-donating ability and a base's proton-accepting ability. Lewis theory, on the other hand, uses the breaking and forming of covalent bonds to describe acid-base characteristics. In this treatment, an acid is an electron pair acceptor and a base is an electron pair donor. Although we can apply Lewis theory to the treatment of acid-base reactions, it is more useful for treating complexation reactions between metal ions and ligands.

The following reaction between the metal ion Cd^{2+} and the **ligand** NH_3 is typical of a complexation reaction.



The product of this reaction is a **metal-ligand complex**. In writing this reaction we show ammonia as $:\text{NH}_3$, using a pair of dots to emphasize the pair of electrons it donates to Cd^{2+} . In subsequent reactions we will omit this notation.

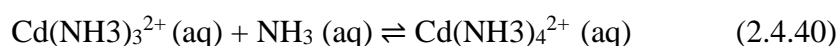
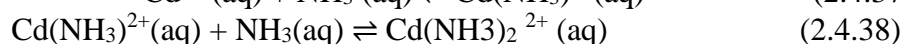
Metal-Ligand Formation Constants

We characterize the formation of a metal–ligand complex by a **formation constant**, K_f . The complexation reaction between Cd^{2+} and NH_3 , for example, has the following equilibrium constant.

$$K_f = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = 5.5 \times 10^7 \quad (2.4.36)$$

The reverse of reaction 2.4.35 is a dissociation reaction, which we characterize by a **dissociation constant**, K_d , that is the reciprocal of K_f .

Many complexation reactions occur in a stepwise fashion. For example, the reaction between Cd^{2+} and NH_3 involves four successive reactions.



To avoid ambiguity, we divide formation constants into two categories. **Stepwise formation constants**, which we designate as K_i for the i th step, describe the successive addition of one ligand to the metal–ligand complex from the previous step. Thus, the equilibrium constants for reactions 2.4.37–2.4.40 are, respectively, K_1 , K_2 , K_3 , and K_4 . Overall, or **cumulative formation constants**, which we designate as β_i , describe the addition of i ligands to the free metal ion. The equilibrium constant in equation 2.4.36 is correctly identified as β_4 , where

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \quad (2.4.41)$$

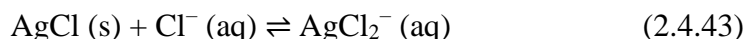
In general

$$\beta_i = K_1 \times K_2 \times \dots \times K_i \quad (2.4.42)$$

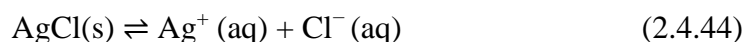
Stepwise and overall formation constants for selected metal–ligand complexes are in [Appendix 12](#).

Metal-Ligand Complexation and Solubility

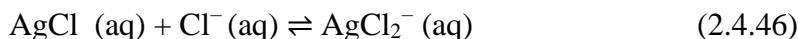
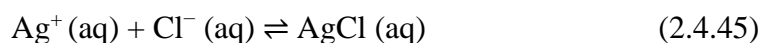
A formation constant characterizes the addition of one or more ligands to a free metal ion. To find the equilibrium constant for a complexation reaction involving a solid, we combine appropriate K_{sp} and K_f expressions. For example, the solubility of AgCl increases in the presence of excess chloride as the result of the following complexation reaction.



We can write this reaction as the sum of three other reactions with known equilibrium constants—the solubility of AgCl, described by its K_{sp}



and the stepwise formation of AgCl_2^- , described by K_1 and K_2 .



The equilibrium constant for reaction 6.4.43, therefore, is $K_{sp} \times K_1 \times K_2$.

Example 2.7

Determine the value of the equilibrium constant for the reaction

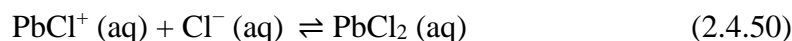
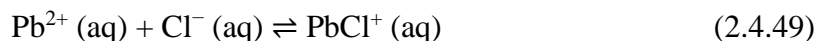


Solution

We can write this reaction as the sum of three other reactions. The first of these reactions is the solubility of $\text{PbCl}_2(\text{s})$, described by its K_{sp} reaction.



The remaining two reactions are the stepwise formation of $\text{PbCl}_2(\text{aq})$, described by K_1 and K_2 .



Using values for K_{sp} , K_1 , and K_2 from [Appendix 10](#) and [Appendix 12](#), we find that the equilibrium constant is

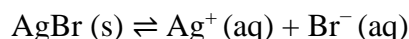
$$K = K_{sp} \times K_1 \times K_2 = (1.7 \times 10^{-5}) \times 38.9 \times 1.62 = 1.1 \times 10^{-3} \quad (2.4.51)$$

Practice Exercise 2.3

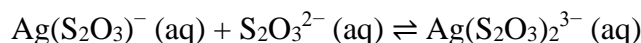
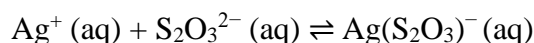
What is the equilibrium constant for the following reaction? You will find appropriate equilibrium constants in [Appendix 10](#) and [Appendix 11](#).



We can write the reaction as a sum of three other reactions. The first reaction is the solubility of AgBr(s), which we characterize by its K_{sp} .



The remaining two reactions are the stepwise formation of $\text{Ag(S}_2\text{O}_3)_2^{3-}$, which we characterize by K_1 and K_2 .

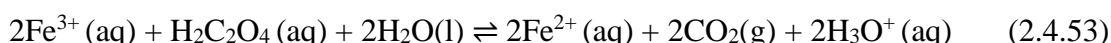


Using values for K_{sp} , K_1 , and K_2 from [Appendix 10](#) and [Appendix 11](#), we find that the equilibrium constant for our reaction is

$$K = K_{\text{sp}} \times K_1 \times K_2 = (5.0 \times 10^{-13})(6.6 \times 10^8)(7.1 \times 10^4) = 23$$

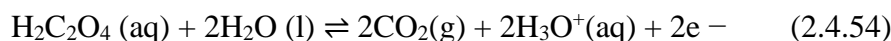
2.4.4 Oxidation–Reduction (Redox) Reactions

An oxidation–reduction reaction occurs when electrons move from one reactant to another reactant. As a result of this electron transfer, these reactants undergo a change in oxidation state. Those reactants that experience an increase in oxidation state undergo **oxidation**, and those experiencing a decrease in oxidation state undergo **reduction**. For example, in the following redox reaction between Fe^{3+} and oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, iron is reduced because its oxidation state changes from +3 to +2.



Oxalic acid, on the other hand, undergoes oxidation because the oxidation state for carbon increases from +3 in $\text{H}_2\text{C}_2\text{O}_4$ to +4 in CO_2 .

We can divide a redox reaction, such as reaction 2.4.53, into separate **half-reactions** that show the oxidation and the reduction processes.



It is important to remember, however, that an oxidation reaction and a reduction reaction occur as a pair. We formalize this relationship by identifying as a **reducing agent** the reactant undergoing oxidation, because it provides the electrons for the reduction half-reaction. Conversely, the reactant undergoing reduction is an **oxidizing agent**. In reaction 2.4.53, Fe^{3+} is the oxidizing agent and $\text{H}_2\text{C}_2\text{O}_4$ is the reducing agent.

The products of a redox reaction also have redox properties. For example, the Fe^{2+} in reaction 2.4.53 can be oxidized to Fe^{3+} , while CO_2 can be reduced to $\text{H}_2\text{C}_2\text{O}_4$. Borrowing some terminology from acid–base chemistry, Fe^{2+} is the conjugate reducing agent of the oxidizing agent Fe^{3+} , and CO_2 is the conjugate oxidizing agent of the reducing agent $\text{H}_2\text{C}_2\text{O}_4$.

Thermodynamics of Redox Reactions

Unlike precipitation reactions, acid–base reactions, and complexation reactions, we rarely express the equilibrium position of a redox reaction using an equilibrium constant. Because a redox reaction involves a transfer of electrons from a reducing agent to an oxidizing agent, it is convenient to consider the reaction's thermodynamics in terms of the electron.

For a reaction in which one mole of a reactant undergoes oxidation or reduction, the net transfer of charge, Q , in coulombs is

$$Q = nF \quad (2.4.56)$$

where n is the moles of electrons per mole of reactant, and F is Faraday's constant (96,485 C/mol). The free energy, ΔG , to move this charge, Q , over a change in **potential**, E , is

$$\Delta G = EQ \quad (2.4.57)$$

The change in free energy (in kJ/mole) for a redox reaction, therefore, is

$$\Delta G = - nFE \quad (2.4.58)$$

where ΔG has units of kJ/mol. The minus sign in equation 6.4.58 is the result of a difference in the conventions for assigning a reaction's favorable direction. In thermodynamics, a reaction is favored when ΔG is negative, but a redox reaction is favored when E is positive. Substituting equation 2.4.58 into equation 2.2.3

$$- nFE = - nFE^\circ + RT \ln Q \quad (2.4.59)$$

and dividing by $-nF$, leads to the well-known **Nernst equation**

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (2.4.60)$$

where E° is the potential under standard-state conditions. Substituting appropriate values for R and F , assuming a temperature of 25°C (298 K), and switching from \ln to \log ($\ln(x) = 2.303\log(x)$) gives the potential in volts as

$$E = E^\circ - \frac{0.05916}{n} \log Q \quad (2.4.61)$$

Standard Potentials

A redox reaction's **standard potential**, E° , provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position. Because a reaction at equilibrium has a ΔG of zero, the potential, E , also must be zero at equilibrium. Substituting these values into equation 6.4.61 and rearranging provides a relationship between E° and K .

$$E^\circ = \frac{0.05916}{n} \log K \quad (2.4.62)$$

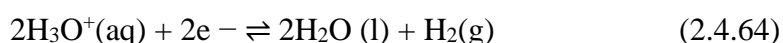
Note : A standard potential is the potential when all species are in their standard states. You may recall that we define standard state conditions as: all gases have partial pressures of 1 atm, all solutes have concentrations of 1 mol/L, and all solids and liquids are pure.

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate E° using the standard potentials for the corresponding oxidation half-reaction and reduction half-reaction. By convention, standard potentials are provided for reduction half-reactions. The standard potential for a redox reaction, E° , is

$$E^\circ = E^\circ_{\text{red}} - E^\circ_{\text{ox}} \quad (2.4.63)$$

where E°_{red} and E°_{ox} are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

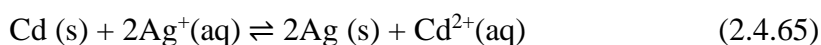
Because we cannot measure the potential for a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference half-reaction and report all other reduction potentials relative to this reference. The reference half-reaction is



Appendix 13 contains a list of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction under standard state conditions. Thus, under standard state conditions the reduction of Cu^{2+} to Cu ($E^\circ = +0.3419$ V) is more favorable than the reduction of Zn^{2+} to Zn ($E^\circ = -0.7618$ V).

Example 2.8

Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential when $[\text{Ag}^+] = 0.020$ M and $[\text{Cd}^{2+}] = 0.050$ M, for the following reaction at 25°C.



Solution

(a) In this reaction Cd is undergoing oxidation and Ag^+ is undergoing reduction. The standard cell potential, therefore, is

$$E^{\circ} = E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = 0.7996 - (-0.4030) = 1.2026 \text{ V} \quad (2.4.66)$$

(b) To calculate the equilibrium constant we substitute appropriate values into equation 2.4.62.

$$E^{\circ} = 1.2026 \text{ V} = \frac{0.05916 \text{ V}}{2} \log K \quad (2.4.67)$$

Solving for K gives the equilibrium constant as

$$\log K = 40.6558 \quad (2.4.68)$$

$$K = 4.527 \times 10^{40} \quad (2.4.69)$$

(c) To calculate the potential when $[\text{Ag}^+]$ is 0.020 M and $[\text{Cd}^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient, Q , in equation 2.4.61.

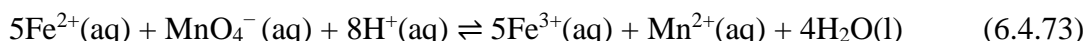
$$E = E^{\circ} - \frac{0.05916 \text{ V}}{n} \log \frac{[\text{Cd}^{2+}]}{[\text{Ag}^+]^2} \quad (2.4.70)$$

$$E = 1.2606 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \frac{(0.050)}{(0.020)^2} \quad (2.4.71)$$

$$E = 1.14 \text{ V} \quad (2.4.72)$$

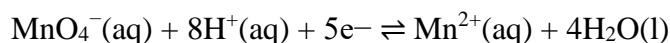
Practice Exercise 2.4

For the following reaction at 25°C



calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: $[\text{Fe}^{2+}] = 0.50 \text{ M}$, $[\text{Fe}^{3+}] = 0.10 \text{ M}$, $[\text{MnO}_4^{-}] = 0.025 \text{ M}$, $[\text{Mn}^{2+}] = 0.015 \text{ M}$, and a pH of 7.00. See Appendix 13 for standard state reduction potentials.

The two half-reactions are the oxidation of Fe^{2+} and the reduction of MnO_4^{-} .



From Appendix 13, the standard state reduction potentials for these half-reactions are

$$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V} \quad E^{\circ}_{\text{MnO}_4^{-}/\text{Mn}^{2+}} = 1.51 \text{ V}$$

(a) The standard state potential for the reaction is

$$E^{\circ} = E^{\circ}_{\text{MnO}_4^{-}/\text{Mn}^{2+}} - E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 1.51 \text{ V} - 0.771 \text{ V} = 0.74 \text{ V}$$

(b) To calculate the equilibrium constant we substitute appropriate values into equation 6.4.62.

$$E^{\circ} = 0.74 \text{ V} = \frac{0.05916}{5} \log K$$

Solving for K gives its value as

$$\log K = 62.5 \quad K = 3.2 \times 10^{62}$$

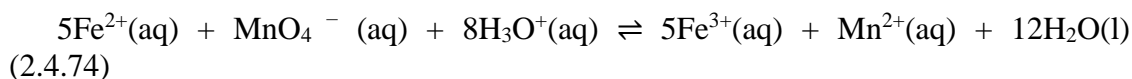
(c) To calculate the potential under these non-standard state conditions, we make appropriate substitutions into the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$$

$$E = 0.74 - \frac{0.05916}{5} \log \frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1 \times 10^{-7})^8}$$

$$E = 0.74 - \frac{0.05916}{5} \log \frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1 \times 10^{-7})^8} = 0.12 \text{ V}$$

Note: When writing precipitation, acid–base, and metal–ligand complexation reaction, we represent acidity as H_3O^+ . Redox reactions are more commonly written using H^+ instead of H_3O^+ . For the reaction in Practice Exercise 6.4, we could replace H^+ with H_3O^+ and increase the stoichiometric coefficient for H_2O from 4 to 12, e.g.,



2.5 Le Chatelier's Principle

The equilibrium position for any reaction is defined by a fixed equilibrium constant, not by a fixed combination of concentrations for the reactants and products. This is easily appreciated by examining the equilibrium constant expression for the dissociation of acetic acid.

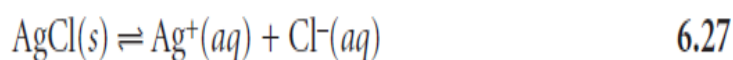
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5} \quad 6.26$$

As a single equation with three variables, equation 6.26 does not have a unique solution for the concentrations of CH_3COOH , CH_3COO^- , and H_3O^+ . At constant temperature, different solutions of acetic acid may have different values for $[\text{H}_3\text{O}^+]$, $[\text{CH}_3\text{COO}^-]$ and $[\text{CH}_3\text{COOH}]$, but will always have the same value of K_a .

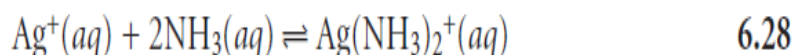
If a solution of acetic acid at equilibrium is disturbed by adding sodium acetate, the $[\text{CH}_3\text{COO}^-]$ increases, suggesting an apparent increase in the value of K_a . Since K_a must remain constant, however, the concentration of all three species in equation 6.26 must change in a fashion that restores K_a to its original value. In this case, equilibrium is reestablished by the partial reaction of CH_3COO^- and H_3O^+ to produce additional CH_3COOH .

The observation that a system at equilibrium responds to a stress by reequilibrating in a manner that diminishes the stress, is formalized as **Le Châtelier's principle**. One of the most common stresses that we can apply to a reaction at equilibrium is to change the concentration of a reactant or product. We already have seen, in the case of sodium acetate and acetic acid, that adding a product to a reaction mixture at equilibrium converts a portion of the products to reactants. In this instance, we disturb the equilibrium by adding a product, and the stress is diminished by partially reacting the excess product. Adding acetic acid has the opposite effect, partially converting the excess acetic acid to acetate.

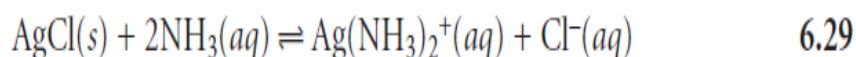
In our first example, the stress to the equilibrium was applied directly. It is also possible to apply a concentration stress indirectly. Consider, for example, the following solubility equilibrium involving AgCl



The effect on the solubility of AgCl of adding AgNO₃ is obvious,* but what is the effect of adding a ligand that forms a stable, soluble complex with Ag⁺? Ammonia, for example, reacts with Ag⁺ as follows



Adding ammonia decreases the concentration of Ag⁺ as the Ag(NH₃)₂⁺ complex forms. In turn, decreasing the concentration of Ag⁺ increases the solubility of AgCl as reaction 6.27 reestablishes its equilibrium position. Adding together reactions 6.27 and 6.28 clarifies the effect of ammonia on the solubility of AgCl, by showing that ammonia is a reactant.

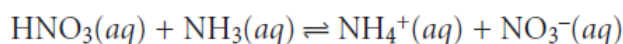


Example 2.9

What is the effect on the solubility of AgCl if HNO₃ is added to the equilibrium solution defined by reaction 6.29?

SOLUTION

Nitric acid is a strong acid that reacts with ammonia as shown here



Adding nitric acid lowers the concentration of ammonia. Decreasing ammonia's concentration causes reaction 6.29 to move from products to reactants, decreasing the solubility of AgCl.



Increasing or decreasing the partial pressure of a gas is the same as increasing its concentration.† The effect on a reaction's equilibrium position can be analyzed as described in the preceding example for aqueous solutes. Since the concentration of a gas depends on its partial pressure, and not on the total pressure of the system, adding or removing an inert gas has no effect on the equilibrium position of a gas-phase reaction.

Equilibrium Constants For Chemical Reactions

Several types of reactions are commonly used in analytical procedures, either in preparing samples for analysis or during the analysis itself. The most important of these are precipitation reactions, acid–base reactions, complexation reactions, and oxidation–reduction reactions. In this section we review these reactions and their equilibrium constant expressions.

Table 2.1 Summarizes the types of chemical constants and equilibrium constants that are importance in analytical chemistry. Simple applications of some of these constants are illustrated in the sections that follow

Equilibria and Equilibrium Constants Important in Analytical Chemistry			
Type of Equilibrium	Name and Symbol of Equilibrium Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$
		$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$	$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$
Formation of a complex ion	Formation constant, β_n	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$\text{I}_2(aq) \rightleftharpoons \text{I}_2(org)$	$K_d = \frac{[\text{I}_2]_{org}}{[\text{I}_2]_{aq}}$

REFERENCES

- Fundamental of Analytical Chemistry, 8th Edition, Skoog.
- Modern of analytical chemistry by David Harvey ([DePauw University](#))