

# Qualitative Chemical Kinetics

## Chapter 17

### In This Chapter

- What is kinetics?
- Energy diagrams
- Factors that affect reaction rates

You're already familiar with the idea that some chemical reactions are fast and some are slow. For example, if you take a match to a log in your fireplace, a slow combustion reaction takes place, causing the log to convert to ashes, water vapor, and carbon dioxide over several hours. On the other hand, if you use the match on a similar mass of gasoline, you get the same amount of fire in a much shorter period of time.

In this chapter, we study chemical reaction rates without all the numbers and fancy equations. Chapter 18 goes into much greater mathematical detail, but it's probably good to ease into the world of kinetics.

### What Is Kinetics?

It's often important to know how quickly a chemical reaction will occur. To do so, we study how quickly the reactants in a chemical process are consumed and how quickly the products are formed. The study of reaction rates is called *kinetics*.

You may notice that this energy diagram looks like a hill. In fact, it behaves much like one, too. Imagine that you're the reactants and you're about to go on an adventure that will transform you into the products. Start at the left side of the diagram (point A) and walk uphill toward the right.

In this particular reaction, your little feet quickly tire as you walk up the hill toward point B because climbing uphill requires energy. In fact, you might say that there's a barrier between you and your destination. Your "energy barrier" (the energy difference between point A and point B) is called the *activation energy* ( $E_a$ ) because you need at least this much energy to be converted into the products of a chemical reaction.



#### DEFINITION

The **activation energy** of a chemical reaction is the minimum amount of energy required for the reactants to be converted into products.

If you don't have enough energy to get to the top of the hill, you'll get too tired to continue and just return to your starting point without changing into anything. During a chemical reaction, you can't just stop in the middle of the reaction and take a break—the reactants either don't do anything or become products.



#### THE MOLE SAYS

You can tell that some reactions require more energy to get started than others. For example, little energy is needed to ignite a piece of paper (a small spark will do it), but a great deal of energy is needed to light a piece of magnesium. Though both reactions give off a lot of energy, the paper lights more easily because its combustion has a lower activation energy.

However, let's say that you have enough energy to climb the hill and reach point B. Point B is called the transition state or activated complex of the chemical reaction because that's the point at which the reactants are halfway to becoming products. This activated complex doesn't look like the reactants of the chemical reaction anymore because the reactants have started to react with each other. But it doesn't look like the finished products, either. Typically, the activated complex of a chemical reaction lasts for only a short period of time because it either finishes reacting to form the desired products or heads back the way it came to regenerate the original reactants.

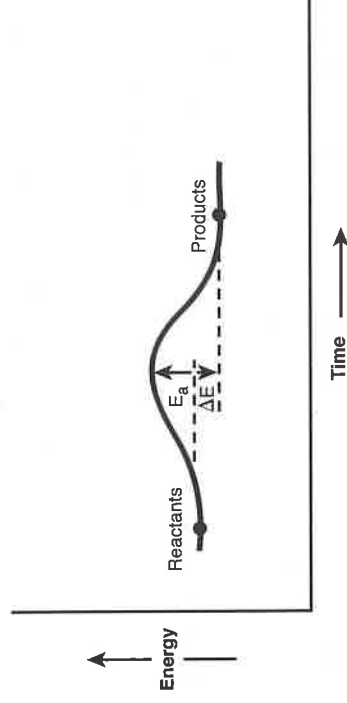


Figure 17.2: The energy diagram for a reversible reaction.

Note that all chemical reactions are reversible to some extent: for all reactions, the products can react to regenerate the reactants. However, if the activation energy for the reverse process is large enough, this reverse reaction is so slow that it's insignificant compared to the forward reaction. Because many reactions fall under this category, the single-headed arrow ( $\rightarrow$ ) is commonly (but incorrectly) used to describe these reactions.

## Factors That Change Reaction Rates

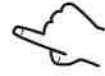
A number of factors can change the rate of a chemical reaction. In this section, we discuss a few of them.

### Temperature

The temperature at which a reaction occurs affects the rates of chemical reactions. For example, if you put a roast in the oven at  $150^{\circ}\text{F}$ , it would take a very, very long time to cook because the process of cooking is slow at low temperatures.

However, imagine that your neighbor came over while you were cooking a  $150^{\circ}\text{F}$  roast and cranked up the temperature to  $500^{\circ}\text{F}$ . As you might expect, the roast would cook much more quickly. By the time the stove alarm went off, you'd have nothing more than a lump of charcoal.

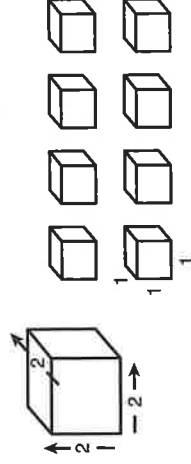
Why do reactions occur more quickly at high temperatures than at low temperatures? As discussed before, the activation energy of a chemical reaction determines the rate of that reaction. Consequently, if the reactants don't have enough energy to form products, the reaction won't go anywhere. When cooking a roast, there simply isn't enough energy at  $150^{\circ}\text{F}$  for the molecules to undergo chemical changes at a useful rate. However, if you increase the energy available to the reactants by increasing the temperature, the molecules in the roast will cook far more quickly.



### CHEMISTRIVIA

Activated charcoal is used in fish filters to remove organic waste. The pieces of charcoal look reasonably large, but they have many small crevices that increase the reactive surface area. As a result, a small amount of activated charcoal can remove a large quantity of dissolved fish poop.

To see that small objects have larger surface areas than large ones, take a look at the accompanying figure, which shows the surface area of an  $8\text{ cm}^3$  cube versus that of eight  $1\text{ cm}^3$  cubes. Both the large cube and the smaller cubes have the same total volume, but they have very different surface areas:



**Figure 17.3:** The surface area of the larger cube is  $24\text{ cm}^2$  and the surface area of the smaller cubes is  $48\text{ cm}^2$ .

By dissolving a reactant, you decrease its size to that of an individual molecule or ion, vastly increasing the reactive surface area so that *all* the reactant particles can potentially react at once. This is why we worried so much in Chapter 15 about which reactants were soluble—the more soluble the reactant, the faster the reaction!



### YOU'VE GOT PROBLEMS

**Problem 3:** Using kinetics, explain why you need to grind coffee beans before you put them in the coffee filter.

## Catalysts

*Catalysts* are materials that increase the rates of chemical reactions without being consumed. Common examples of catalysts are platinum (used in automobile catalytic converters) and the enzymes in your body that cause biochemical reactions to occur more quickly.

**CHEMISTRIVIA**

Inhibitors are chemicals that do the opposite of catalysts: they slow or stop reactions.

**The Least You Need to Know**

- Kinetics is the study of chemical reaction rates.
- Energy diagrams show how the energies of the reactants change during a chemical reaction.
- All reactions are reversible, but in many cases, the backward reaction is so much slower than the forward reaction that it is *effectively* irreversible. When the concentrations of product and reactant remain constant, the system is said to be at equilibrium.
- Temperature, reactant concentration, surface area, and catalysts all can change the rates of a chemical reaction.

# Quantitative Chemical Kinetics

## Chapter

# 18

### In This Chapter

- Differential rate laws
- Integrated rate laws
- Half-lives
- The Arrhenius equation
- Reaction mechanisms

Now that you understand why things happen in a qualitative sense, it's time to explain chemical rates in numerical terms. It's nice to know that you can make a reaction occur more quickly by heating it, but it's even nicer to know how long that process is likely to take. After all, it's great to double a reaction rate, but if it cuts the reaction time from 10 weeks to 5 weeks, you're still going to be sitting around twiddling your fingers and toes while you wait for it to finish.

Fortunately, you can use some tricks to make this process easier. By the time you finish this chapter, you'll be a kinetics pro!

## What Are Rate Laws?

Rate laws are expressions that show how the rate of a chemical reaction depends on the concentration or temperature of the reactants. Two types of rate laws are commonly discussed: differential rate laws and integrated rate laws. When reading this chapter, keep in mind that both types of rate laws are derived from the same information, but they're written in different forms to solve different types of problems.

**Example:** You've found the initial rates of a chemical reaction ( $A + B \rightarrow C$ ) with the following initial concentrations of compound A and B:

Experiment	[A](M)	[B](M)	Initial Rate (M/s)
1	0.0100	0.0100	$3.00 \times 10^{-5}$
2	0.0200	0.0100	$6.00 \times 10^{-5}$
3	0.0100	0.0200	$6.00 \times 10^{-5}$

Using this experimental information, determine the rate law for this reaction, the value of the rate constant  $k$ , and the initial rate of the reaction when the concentration of compound A is 0.0500 M and the concentration of compound B is 0.0400 M.

**Solution:** Before getting started with this problem, we should point out something that's pretty neat. Imagine yourself as a chemist who has set up this reaction  $A + B \rightarrow$  and done three quick kinetic experiments (the data for which is shown in the minitable). With this little bit of experimentation, you can now figure out the rate of this reaction no matter what the concentrations of the reactants are, even if they're nowhere near what your original experiments measured. Pretty cool, eh?



#### THE MOLE SAYS

The rate constant ( $k$ ) for a reaction doesn't change when the concentrations of the reactants are changed. However, changing the concentrations of the reactants changes the rate of a chemical reaction because of the  $[A]$  and  $[B]$  terms in the rate equation.

To find the rate law, use the following equation:

$$\text{Rate} = k[A]^x[B]^y$$

From the initial data, you can see that the rate doubled between experiment 1 and experiment 2. This occurred because you doubled the concentration of A. Because the reaction rate is directly proportional to A, the reaction is first order with respect to A, making  $x = 1$ .

Likewise, the reaction rate doubled between experiments 1 and 3 when the concentration doubled with respect to B. As a result, the reaction is first order with respect to B (that is,  $y = 1$ ).

## Integrated Rate Laws

The second main type of rate law describes how the concentrations of the reactants change as the reaction progresses. These are commonly referred to as *integrated rate laws*. Let's take a look at how to determine the integrated rate law for chemical reactions.



### DEFINITION

**Integrated rate laws** describe how the concentrations of the reactants in a chemical reaction change over time.

## First-Order Integrated Rate Laws

Let's say that you're studying the rate of reaction  $A \rightarrow B$  and that you've already determined that this is a first-order reaction using the methods you learned in the previous section. The rate law for this first-order reaction is:

$$\text{Rate} = k[A]$$

You need to manipulate this equation in such a way that you can relate the concentration of reactant A to the amount of time that the reaction has been proceeding. Some bad news: this requires calculus. Fortunately, I don't really feel like doing any calculus today, so I'll just tell you that this is the result of all that crazy math:

$$\ln[A] = -kt + \ln[A_0]$$

$k$  is the rate constant of this reaction,  $t$  is the amount of time since the reaction started (in seconds),  $[A_0]$  is the initial concentration of reactant A, and  $[A]$  is the concentration of reactant A after  $t$  seconds have elapsed.

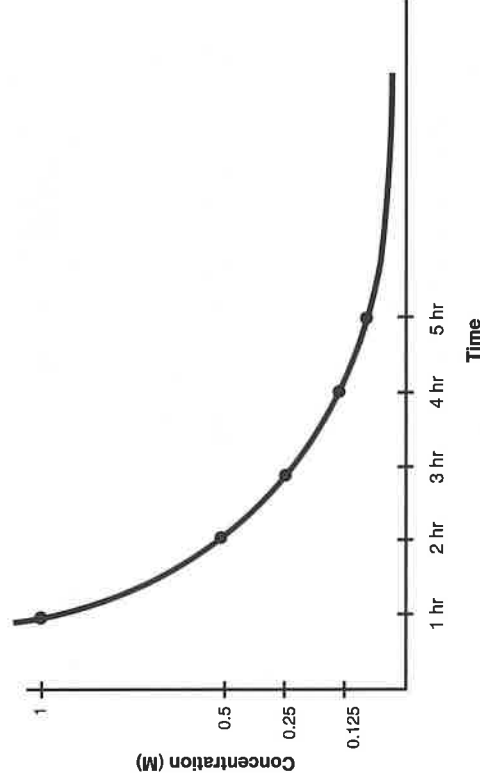


### CHEMISTRIVIA

For those of you who don't remember this from your math class, the term *ln* stands for natural logarithm. In this context,  $\ln[A]$  means "to find the natural logarithm of the concentration of A using the ln button on your calculator."

This equation is really neat for the following reasons:

- It allows you to determine how the concentration of your reactant changes as the reaction proceeds—as long as you know the initial concentration of the reactant ( $[A_0]$ ), the time ( $t$ ), and the rate constant ( $k$ ).



**Figure 18.1:** A graph showing the half-lives for a chemical reaction. Though the concentration of the reactants decreases, the half-life stays the same over the life of the reaction for first-order processes.

To determine the half-life of a first-order chemical reaction, you use the same equation you used to determine the relationship between concentration and time:

$$\ln[A] = -kt + \ln[A_0]$$

At  $t = t_{1/2}$ , the concentration of A is exactly half of what it originally was,  $[A_0]/2$ . When you substitute  $[A_0]/2$  for  $[A]$  in this equation and rearrange, you ultimately end up with this:

$$t_{1/2} = \frac{0.693}{k}$$

This equation allows you to relate the half-life of a reaction to the rate constant. This is useful to chemists because it's nice to know ahead of time if the reaction you're planning on performing will be only half-finished three years from now.



#### THE MOLE SAYS

Incidentally, if you don't care about the half-life of a reaction but you want to know when the reaction will be 95 percent finished, you can plug the appropriate numbers into the equation  $\ln[A] = -kt + \ln[A_0]$ .

For second-order reactions, the half-life is no longer constant. In other words, if the first half-life of a reaction is 10 minutes, the second half-life will be something different. Because this is more complicated than we really want to worry about here, we're not going to worry about it.

## Zero-Order Integrated Rate Laws

Sometimes the rate of a chemical reaction doesn't depend at all on the concentration of the reagent. This is particularly common for reactions involving catalysts because the quantity of catalyst present determines the reaction rate. In such a case, this is the integrated rate law:

$$\text{Rate} = k[A]^0 = k$$

Simply put, the rate is equal to the rate constant because anything raised to the zeroth power is 1.



### CHEMISTRIVIA

What about third-, fourth-, and fifth-order reactions? Well, we don't normally worry about them much because they aren't very common. You see, for a reaction to have a fifth-order rate expression, five different molecules would have to hit each other simultaneously with the right amount of energy to become products. This never really happens, for the same reason that car accidents never have five cars hitting each other simultaneously—it's just too unlikely!

## The Dependence of Reaction Rate on Temperature

In Chapter 17, we discussed how increased temperatures cause the rate of a chemical reaction to increase. We explained this by saying that, as reactant temperature increases, more of the molecules have the required activation energy for the reaction to take place.

In 1889, the Swedish chemist Svante Arrhenius was studying the dependence of reaction rate on temperature and discovered that most reaction rate data fits the following equation:

$$k = Ae^{-E_a/RT}$$

**Example:** The reaction  $A + B \rightarrow C$  has a rate constant of  $1.20 \text{ L/mol}\cdot\text{s}$  at  $140^\circ\text{C}$  and a rate constant of  $2.50 \times 10^5 \text{ L/mol}\cdot\text{s}$  at  $340^\circ\text{C}$ . Given that  $R = 8.31 \text{ J/K}\cdot\text{mol}$ , what is the activation energy of this reaction?

**Solution:** From the information given, you can see that  $T_1 = 413 \text{ K}$  ( $140^\circ\text{C} + 273$ ),  $k_1 = 1.20 \text{ L/mol}\cdot\text{s}$ ,  $T_2 = 613 \text{ K}$  ( $340^\circ\text{C} + 273$ ), and  $k_2 = 2.50 \times 10^5 \text{ L/mol}\cdot\text{s}$ . Substituting these values and the value of  $R$  into the preceding equation, you find:

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{2.50 \times 10^5 \text{ L/mol}\cdot\text{s}}{1.20 \text{ L/mol}\cdot\text{s}}\right) = \left(\frac{E_a}{8.31 \text{ J/K}\cdot\text{mol}}\right)\left(\frac{1}{413 \text{ K}} - \frac{1}{613 \text{ K}}\right)$$

$$E_a = 1.29 \times 10^5 \text{ J/mol}$$



#### YOU'VE GOT PROBLEMS

Problem 4: For the reaction  $A + B \rightarrow C$ , the rate constant at  $800^\circ\text{C}$  is  $2.50 \text{ L/mol}\cdot\text{s}$  and the rate constant at  $850^\circ\text{C}$  is  $12.2 \text{ L/mol}\cdot\text{s}$ . Given that  $R$  is  $8.31 \text{ J/K}\cdot\text{mol}$ , what is the activation energy for this reaction?

## Reaction Mechanisms

In what order do the reactants combine with one another in a chemical reaction? Read on to find out how you can figure this out.

### An Introduction to Reaction Mechanisms

Now that we've discussed rate laws in great gory detail, it's time to learn how to use them to figure out the way in which the reactants in a chemical process form products. The method by which a reaction takes place is known as the *reaction mechanism*.



#### DEFINITION

The **reaction mechanism** for a chemical process describes the order in which the reactants combine with each other to form products. You can usually determine this mechanism by examining the kinetic data for a reaction.

Now, you might expect the overall rate laws for a multistep process to be difficult to understand. After all, if you have two elementary reactions in a mechanism, don't you have two rate laws to keep track of at once?

Not necessarily. Let's go back to the scrambled egg-making example:

**Step 1:** Raw eggs in shell  $\rightarrow$  Raw egg goo + Yucky shells

**Step 2:** Raw egg goo + Milk + Butter  $\rightarrow$  Scrambled eggs

Which process is faster? If you've made scrambled eggs, you know that cracking an egg is a fast process, yet it takes quite a while to actually cook it into something edible. As a result, the speed at which you crack the eggs has little to do with how fast the eggs are made—the much slower rate at which you can cook the eggs determines the speed of this process.

In a reaction with several elementary steps, the slowest step is called the *rate-determining step* or *rate-limiting step* because it alone is responsible for the observed overall rate of the chemical reaction.

## Proposing a Reaction Mechanism

Getting back to the main point of this topic, how can you use rate laws to determine the mechanism for a chemical reaction? Consider the following process:



Now, nobody's sure how this process actually occurs, but it is known that the overall reaction rate can be expressed by the following equation:

$$\text{Rate} = k[B]$$

Now, I've got a theory. My theory says that the reaction proceeds via the following mechanism:

**Step 1:**  $2 A \rightarrow Y + D$       Slow process

**Step 2:**  $B + D \rightarrow A + Z$       Fast process

How do I know whether my theory is correct?

## The Least You Need to Know

- Rate laws are expressions that show how the rate of a chemical reaction depends on the concentrations of the reactants or the time elapsed since the reaction began.
- The half-life of a reaction is the period of time required for half of the reactants to be converted into products.
- The Arrhenius equation is used to determine the relationship between rate and temperature.
- Reaction mechanisms describe the process by which the reactants in a chemical process are converted to products.

# The World of Chemical Equilibria

## Chapter

# 19

### In This Chapter

- Equilibrium constants
- Heterogeneous equilibria
- Reaction quotients
- Le Châtelier's principle

Chapter 17 briefly mentioned that chemical reactions can sometimes run backward as well as forward, causing the products of the reaction to regenerate the reactants. However, we then discussed reactions as if they went only in the forward direction. We could get away with this because many chemical reactions go mostly forward, with only the tiniest smidgen of backward reaction.

Well, boys and girls, it's time to stop ignoring the backward reaction! In this chapter, you learn all about chemical equilibria. Hold on to your hats!

### What Is an Equilibrium?

Back in Chapter 17, when we discussed energy diagrams, we mentioned that chemical reactions can move in the backward direction as well as the forward direction, forming reactants from the products. Such a reaction is referred to as being reversible and has the general form  $A \rightleftharpoons B$ .

In Chapter 18, you learned that, as the concentration of the reactants increases, the rate of the reaction increases. As you might imagine, the same is true for the products, and the reverse reaction speeds up as the concentrations of the products increase. As a result, the concentrations of the reactants and products in a reversible reaction change in the following way over time.

What the law of mass action says is simple. Let's say that you have a reaction taking place in solution with the following equation:



The equilibrium condition can be expressed using the following equation:

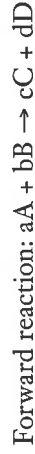
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$K_{eq}$  is the equilibrium constant for this process, each of the letters in the brackets stands for the concentration of that chemical in mol/L (a.k.a.  $M$ ) when the reaction has reached equilibrium, and the superscripts stand for the coefficient of each chemical. For gases, the equilibrium constant is determined in almost the same way, except that partial pressures are used in place of concentrations.

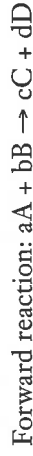
The equilibrium constant is important because it gives you an idea of where the equilibrium lies. The larger the equilibrium constant, the farther the reaction lies toward the products. For example, an equilibrium constant of  $1.0 \times 10^{-6}$  suggests that you have mostly reactants in the mixture (that is, the equilibrium lies toward the reactants), and an equilibrium constant of  $1.0 \times 10^6$  suggests that you've mostly converted reactants to products (that is, the equilibrium lies toward the reactants).

## Hold On a Sec: Where'd That Fancy Equation Come From?

I thought you'd never ask! Let's consider the two reactions that are occurring in the previous process. The first is the forward reaction, and the second is the reverse reaction:



Now, you learned back in Chapter 18 how to find the rate expression for a chemical reaction. You can assume that each reaction occurs in only one step and isn't some complicated mechanism, to make life easier. Making the rate expressions sounds like so much fun, so let's go ahead and do it:



$$\text{Forward rate} = k_f[A]^a[B]^b$$



$$\text{Reverse rate} = k_r[C]^c[D]^d$$

To find the value for the equilibrium constant for this reaction, just plug the experimental data you were given into this expression:

$$K_{eq} = \frac{[3.5 \times 10^{-3} M][3.5 \times 10^{-3} M]}{[0.68 M]}$$

$$K_{eq} = 1.8 \times 10^{-5}$$

## Using Equilibrium Constants to Solve Problems

Once you have an equilibrium constant, you can use it to figure out what the equilibrium concentrations of the products will be, given an initial concentration of the reactants. Consider an example.

**Example:** Given the previous reaction, what will be the equilibrium concentration of the  $H^+$  ion if the initial concentration of acetic acid is 1.00 M and the equilibrium constant is  $1.8 \times 10^{-5}$ ?

**Solution:** Let's walk through this process step by step. You already have the equilibrium expression for this process from the last problem. Now all you need to do is figure out what concentrations to stick into it. To do this, you need to be creative. I don't know about you, but when I get creative, I like to make a chart.

Species	Initial Concentration	Concentration Change	Final Concentration
$C_2H_3O_2H$	1.00 M	$-x$	$(1.00 - x) M$
$H^+$	0	$x$	$x M$
$C_2H_3O_2^-$	0	$x$	$x M$

Huh? Let's talk about where all the numbers in this chart come from.

- The initial concentration of acetic acid is defined by the problem as 1.00 M. Between the time the reaction starts and the time the system reaches equilibrium, some of it will turn into products. We don't have any idea how much of it will actually do this, so let's just admit that  $x$  amount of it goes away, making the change  $-x$ . As a result, the final concentration is equal to the initial concentration minus the change, or  $(1.00 - x)M$ .
- The initial concentrations of both  $H^+$  and the acetate ion are zero because neither is present until the acetic acid starts dissociating. However, from the equation, you can see that every time a molecule of acetic acid breaks apart, one  $H^+$  ion and one acetate ion are formed. As a result, if the concentration of acetic acid

## Heterogeneous Equilibria

All the equilibria we've been talking about so far have chemical species in the same phase. For solutions, they're all dissolved, and for gaseous equilibria, they're all gases. Equilibria in which all species are in the same phase are called *homogeneous equilibria*.

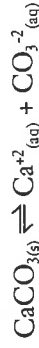
However, we can also talk about equilibria in which not all the species are in the same phase. These equilibria are referred to as *heterogeneous equilibria*. An example of a heterogeneous equilibrium is an ionic compound that partially dissolves in water.



### DEFINITION

A **homogeneous equilibrium** occurs when all reagents and products are found in the same phase (solid, liquid, or gas). A **heterogeneous equilibrium** occurs when they are in different phases.

To demonstrate what a heterogeneous equilibrium looks like, we'll discuss the equilibrium expression for when calcium carbonate dissolves in water (a process known as dissociation). The equation for this process is:



Let's write the equilibrium expression for this process:

$$K_{sp} = \frac{[\text{Ca}^{+2}][\text{CO}_3^{-2}]}{[\text{CaCO}_3]}$$



### THE MOLE SAYS

The  $K_{sp}$  in this equilibrium expression stands for solubility product constant. There's no conceptual difference between this and any other equilibrium constant. The only difference is that the little "sp" at the bottom denotes that you're trying to dissolve something.

However, there's a twist. Recall that any time you put something in square brackets, you need its concentration. Because  $\text{CaCO}_3$  is a solid in this process, it doesn't have a concentration and doesn't really take part in the equilibrium. As a result, you just leave it out of the equilibrium expression. (I'll bet you wish you could do that with everything that didn't make sense!) Likewise, whenever you have a pure solid or a pure liquid (but not a solution) in equilibrium, you leave it out of the expression for  $K_{eq}$  or  $K_{sp}$ .

Le Châtelier's principle states that if you change the conditions of an equilibrium process, the equilibrium will shift in a way that minimizes the effect of whatever you did.



#### THE MOLE SAYS

Le Châtelier's principle states that, when disturbed, an equilibrium shifts to minimize the effects of whatever you did. However, it's important to note that the concentrations of the chemical species will be different in the new equilibrium than they were before the equilibrium was disturbed. In essence, a new equilibrium is created to maintain  $K_{eq}$  for the reaction.

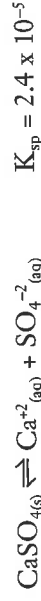
In other words, equilibria are like obnoxious little kids. For example, if you yell at a little kid, the kid will change his behavior to minimize your yelling. Likewise, if you change the conditions of an equilibrium, the equilibrium will shift in a way that partially undoes whatever you did to it in the first place.

## Changes in Concentration

Le Châtelier's principle says that if you change the concentration of one of the compounds in an equilibrium, the position of the equilibrium will also change.

For example, if the process  $A + B \rightleftharpoons C$  is at equilibrium, you can disturb the equilibrium by adding a bunch of compound A to the reaction. To minimize the effects of the added A, the equilibrium shifts in such a way that it decreases the amount of compound A—namely, it produces more of compound C. Likewise, by adding more of compound C, the equilibrium is pushed toward the reactants, making more of A and B.

This phenomenon often happens when an ionic compound dissolves. Let's see an example:



Doing the math you learned earlier in this chapter, you can easily find the equilibrium concentration of the calcium ion:

$$K_{sp} = 2.4 \times 10^{-5} = [x][x]$$

$$x = 4.9 \times 10^{-3} \text{ M}$$

If you increase the pressure of this mixture of gases by squishing it into a smaller area, the pressure of each of the gases increases. Le Châtelier's principle states that equilibria want to decrease the effects of any changes, so the equilibrium will shift in a way that reduces the overall pressure of the system. The only way to accomplish this is to have fewer moles of gas present. As a result, the reaction shifts toward products, to reduce the overall pressure.

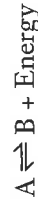


#### BAD REACTIONS

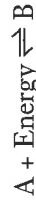
There's another way to increase the pressure of a gaseous mixture: add another gas that has nothing to do with the equilibrium. Though the overall pressure in the container increases, the partial pressures of each gas does not. As a result, the addition of another gas doesn't change the position of the equilibrium.

## Change in Temperature

Some reactions naturally give off energy (they're exothermic), and some reactions require energy to take place (they're endothermic). If you think of the energy in an exothermic reaction as being a product, the reaction  $A \rightleftharpoons B$  has the form:



Likewise, in an endothermic reaction, you can think of energy as a reagent:



When you increase the temperature of a chemical reaction, you're really adding energy to it. You can think of energy as being either a reactant or a product, so the addition of extra energy disrupts the equilibrium. For exothermic reactions, the addition of energy pushes the reaction toward the reactants. For endothermic reactions, the addition of energy pushes the reaction to the right, toward the products.



#### YOU'VE GOT PROBLEMS

Problem 3: Determine qualitatively how the following changes affect the following equilibrium:  $A_{(g)} + 2 B_{(g)} \rightleftharpoons 2 C_{(g)} + \text{Energy}$

- Some of the product C is removed from the mixture.
- 2 atm of compound D (also a gas) are added to the mixture.
- The mixture is squished into a much smaller container.
- The temperature of the mixture decreases.

# Practical Chemistry

We've finally gotten to the good part of chemistry! Instead of being content just talking about equations and phases of matter, we're at the part where you get to start fires and blow stuff up. At least, that's what always seems to happen when I get into the lab.

If you're interested in seeing what sorts of specific reactions chemists like to play with in their labs, keep reading!

# Acids and Bases

## In This Chapter

- The three definitions of acids and bases
- The pH scale
- Titrations
- Buffers

As you learned in Chapter 15, acid-base reactions have equations with the general form  $\text{HA} + \text{BOH} \rightleftharpoons \text{BA} + \text{H}_2\text{O}$ . So far, that's really all we've said about them. As you probably guessed, there's a lot more to acids and bases than this equation.

The reason acid-base reactions are so important is that many of the things you come into contact with on a daily basis are either acidic or basic. Most fruits are acids, as are carbonated beverages, tea, and battery acid. Common household bases include baking soda, ammonia, soap, and antacids. As you'll find, acids and bases really aren't that hard to understand when you get the hang of them.

## What Are Acids and Bases?

Although acids and bases aren't that hard to understand, we have some bad news: not one, but *three* common definitions are used to describe acids and bases—the Arrhenius definition, the Brønsted-Lowry definition, and the Lewis definition. Though this makes it sound as if you'll have to learn about acids and bases three times, the good news is that, for many practical purposes, these three definitions are equivalent.

*Arrhenius bases* are compounds that cause the formation of the hydroxide ion when placed in water. One example of an Arrhenius base is sodium hydroxide (NaOH):



Bases frequently have “OH” in their formulas, although there are exceptions. For example, ammonia (NH<sub>3</sub>) doesn’t contain hydroxide ions, but forms them when it reacts with water:



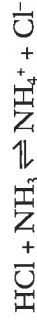
#### THE MOLE SAYS

Some oxides form acids or bases when water is added. Because these compounds don’t contain any H<sup>+</sup> or OH<sup>−</sup> ions unless they react with water, they’re called anhydrides. Typically, oxides of nonmetals are acid anhydrides (they form acid when placed in water), and oxides of metals are base anhydrides.

## Brønsted-Lowry Acids and Bases

In the early 1900s, Johannes Brønsted and Thomas Lowry proposed an alternate definition for acids and bases. This new theory was devised to account for the fact that ammonia can neutralize the acidity of an acid—making it a base—even if water isn’t present.

A *Brønsted-Lowry acid* is a compound that gives hydronium ions to other compounds. For example, HCl is a Brønsted-Lowry acid because it gives H<sup>+</sup> ions to compounds that it reacts with. *Brønsted-Lowry bases* are compounds that can accept hydronium ions. For example, when ammonia gets a hydronium ion from HCl, it forms the ammonium ion:



In this reaction, you can see that hydrochloric acid acts as an acid because it gives H<sup>+</sup> to ammonia. Likewise, ammonia acts as a base because it accepts that proton from HCl.

However, if you look at the other side of the equation, you find the chloride and ammonium ions. Because the chloride ion can accept a proton from the ammonium ion (to re-form HCl), the chloride ion acts as a weak Brønsted-Lowry base. Because the ammonium ion has an extra proton to donate (in this case, to the chloride ion), it is a Brønsted-Lowry acid.

One way of looking at this process is that the ammonia atom is donating its lone pair to the proton. Because the lone pairs are driving this chemical reaction, you have a new definition of acidity and basicity called Lewis acidity/basicity. A *Lewis base* is a compound that donates an electron pair to another compound (the ammonia in our example), and a *Lewis acid* is a compound that accepts an electron pair (the  $H^+$  ion in our example). Though ammonia donated a lone pair to a proton in the example, the lone pair in ammonia can react with a lot of other compounds as well. For example, ammonia can donate its lone pair of electrons to  $BH_3$ , by the following process:

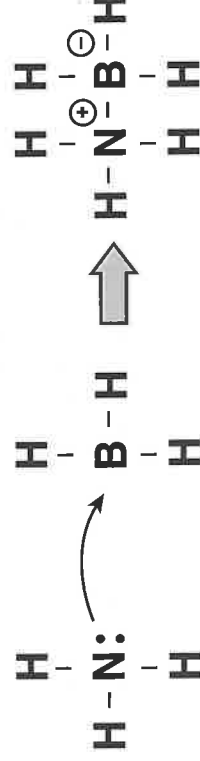


Figure 20.3: The lone pair on ammonia (the Lewis base) is donated to boron in  $BH_3$  (the Lewis acid).

Generally, the Lewis definition of acids and bases is the most useful because it is the most inclusive of the three. For example, the Brønsted-Lowry definition of an acid includes  $HF$  but not  $BH_3$ , because  $BH_3$  doesn't lose a proton when attacked by the lone pairs on a Lewis base.



#### DEFINITION

**Arrhenius acids** give off hydronium ( $H^+$ ) ions in water, and **Arrhenius bases** give off hydroxide ions.

**Brønsted-Lowry acids** give  $H^+$  ions to **Brønsted-Lowry bases**, which accept them.

**Lewis bases** donate electron pairs to **Lewis acids**, which accept them.

## Properties of Acids and Bases

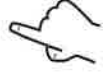
It's frequently possible to tell acids and bases apart by some of their easily observed chemical and physical properties. This table compares these properties.



### CHEMISTRIVIA

Nobody's really sure what "pH" stands for. Some people think it means "power of hydrogen," whereas others think it's either "potential of hydrogen" or "percentage of hydrogen." Personally, I like the idea of calling on the "power of hydrogen" when I'm in trouble.

The pH of a solution can be found experimentally in several ways. The most common way you're likely to encounter is an indicator, which turns one color in acidic solutions and another in basic solutions. The most frequently used indicators are litmus (red = acid, blue = base) and phenolphthalein (pronounced "fee-no-thay-leen"; colorless = acid, pink = base).



### CHEMISTRIVIA

In addition to being a widely used indicator, phenolphthalein was the most common over-the-counter laxative until it was banned in 1999 as a potential carcinogen.

## Finding the pH of a Strong Acid

*Strong acids* are acids that nearly completely *dissociate* when placed in water. That is, almost every molecule of the acid HA breaks up into  $H^+$  and  $A^-$  ions. Some common strong acids include HCl, HBr, HI,  $HNO_3$ ,  $H_2SO_4$ , and  $HClO_4$ .



### DEFINITION

**Strong acids** almost completely **dissociate** (break apart) in water to form  $H^+$  and  $A^-$  ions.

Because strong acids completely dissociate in water, the concentration of  $H^+$  in solution is the same as the concentration of the acid you started with. For example, the pH of a 0.00500 M HCl solution is the following:

$$-\log(0.00500 \text{ M}) = 2.30$$



### YOU'VE GOT PROBLEMS

Problem 3: What is the pH of the following solutions?

- A solution in which 1.00 grams of  $HNO_3$  are present in 25.0 L of the acidic solution?
- A solution made by diluting 3.75 mL of 0.250 M HCl to a final volume of 1,500 mL?

To determine the concentration of the species in this equation, you need to set up the expression for the equilibrium constant:

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

Initially, the concentration of acetic acid is 0.500 M. Take a look at this chart to see how the concentrations of everything changes during the dissociation process. If you're not sure where these values come from, go back to Chapter 19, as I suggested.

Chemical Species	Initial Concentration (M)	Change in Concentration (M)	Final Concentration (M)
CH <sub>3</sub> COOH	0.500	-x	0.500 - x
CH <sub>3</sub> COO <sup>-</sup>	0	x	x
H <sup>+</sup>	0	x	x

Putting these values into the previous equilibrium expression, you get:

$$1.75 \times 10^{-5} = \frac{[x][x]}{[0.500]}$$

Because acetic acid is a weak acid with a low equilibrium constant, we assume that  $x$  is a small value when compared to 0.500 M. This enables you to eliminate the  $x$  in the denominator (bottom part) of this equation because  $[0.500 - (\text{a very small number})]$  is roughly equal to 0.500.

$$1.75 \times 10^{-5} = \frac{[x][x]}{[0.500]}$$

$$x = 0.00296\text{M}$$

This tells you that the concentrations of the H<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> ions are 0.00296 M. To find the pH, all you need to do is to place this value for [H<sup>+</sup>] into the equation for pH:

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(0.00296)$$

$$\text{pH} = 2.53$$

**Solution:** Using the equilibrium expression for water and replacing the values with what you know, you get the following:

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

$$1.00 \times 10^{-14} = [\text{H}^+][0.0500]$$

$$[\text{H}^+] = 2.00 \times 10^{-13} \text{ M}$$

From here, you simply find the pH as you did before:

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(2.00 \times 10^{-13})$$

$$\text{pH} = 12.7$$

This answer indicates a basic solution, which is what you would expect from a 0.0500 M NaOH solution.



#### YOU'VE GOT PROBLEMS

Problem 5: What's the pH of a 0.00340 M LiOH solution?

Problem 6: What's the pH of a 0.00500 M  $\text{NH}_4\text{OH}$  solution?  $K_b(\text{NH}_4\text{OH}) = 1.79 \times 10^{-5}$ .

## Titration

I found a bottle in the stockroom of my lab a few years back. When I opened it, I knew from the burning smell that it was a bottle of nitric acid. However, I had absolutely no idea what the concentration of this acid was, and without this information, it's hard to find a use for it.



#### DEFINITION

A **titration** occurs when you perform a neutralization reaction to determine the concentration of an acid or a base.

Fortunately, I had a way to solve this problem. As mentioned in Chapter 15, acid-base reactions occur when an acid and base combine by the following general equation:



This indicates that the nitric acid in my lab had a concentration of 2.09 M. Why anybody would make a solution with this molarity, I have no idea.



#### YOU'VE GOT PROBLEMS

Problem 7: If it takes 25 mL of 0.500 M HCl to neutralize 175 mL of a NaOH solution, what is the concentration of the NaOH solution?

## Buffers

Your blood is a slightly basic solution. Consider what happens when you drink a big bottle of soda (pH  $\sim$  3):

- The acid in the soda neutralizes the small amount of base in your blood.
- The remaining acid in the soda causes the pH of your blood to decrease rapidly to a pH of about 5.
- The enzymes in your body stop working and you die a horrible, painful death.

Okay, maybe that's not what happens when you drink a soda. However, if something in your blood didn't stabilize its pH, that's exactly what would happen.

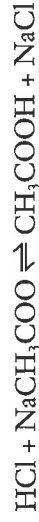
Your blood, like many solutions, is a buffer. *Buffers* are solutions consisting of a weak acid and its conjugate base—these solutions resist changes in pH when either acids or bases are added to them.



#### DEFINITION

**Buffers** are solutions that resist changes in pH when acids or bases are added to them. They consist of weak acids and their conjugate bases.

Imagine that you have a buffered solution that contains acetic acid as its weak acid and sodium acetate as its conjugate base. If you added some hydrochloric acid to this solution, the sodium acetate would react with it by the following process:



As you can see, the strong HCl that was added to the solution was converted to acetic acid, which is a weak acid. Because weak acids cause a much smaller disruption in pH than strong acids, the pH of the solution will decrease much less than if it contained no sodium acetate.

### The Least You Need to Know

- The three definitions used to describe acids and bases are the Arrhenius definition, the Brønsted-Lowry definition, and the Lewis definition.
- The pH scale is commonly used to describe the acidity of solutions.
- A titration is the use of a neutralization reaction to find the concentration of an acid or base.
- Buffers are mixtures of weak acids and their conjugate bases that resist changes in pH.

# Electrochemistry

## In This Chapter

- Oxidation states
- Redox reactions
- Voltaic cells
- The Nernst equation
- Electrolytic cells

When I was in first grade, a “friend” of mine told me that something neat would happen if I placed the two terminals of a 9-volt battery to my tongue. That day, I learned about electrochemical reactions in a way that was less than fun, what with the pain in my tongue and all.

I guess that’s a roundabout way of saying that electrochemistry is all around us. From the batteries we shock ourselves with to the electroplating process that we use to cover cheap jewelry with a microscopically thin veneer of gold, electrochemistry is a part of life. It’s time you learned more about it!

## Oxidation States

Before we can talk about how electrochemical reactions occur, we need to work through the basics. In electrochemistry, nothing is more basic than the concept of oxidation states.

*Oxidation states* describe the charges that the atoms in chemical compounds are considered to have. In simple ionic compounds, the oxidation states of cations and anions are the same as their charges (for example, in NaCl, the oxidation state of sodium is +1 and the oxidation state of chlorine is -1). However, for covalent compounds and polyatomic ions, you need to turn to other rules for help.

gains electrons, causing it to have a more negative oxidation state, it has been *reduced*. Reactions in which oxidation and reduction occur are called oxidation-reduction reactions, or more commonly *redox reactions*.

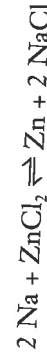


### DEFINITION

An atom has been **oxidized** if it loses electrons and **reduced** if it gains electrons. Reactions in which the oxidation states of the elements change are called **redox reactions**.

To keep oxidation and reduction clear in your head, use the following phrase: **Larry Eats Oranges; Gina Eats Rabbits**. The first letters in this phrase, LEO-GER, tells you that losing electrons = oxidation (LEO), gaining electrons = reduction (GER).

Let's take a look at a sample redox reaction and determine which elements have been oxidized and reduced:



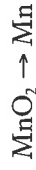
- On the reactant's side of the equation, sodium has an oxidation state of zero because it is a pure element. On the product's side of the reaction, it has an oxidation state of +1. Sodium has been oxidized because its charge has been made more positive (0 to +1) through the loss of electrons.
- On the reactant's side of the equation, zinc has a +2 oxidation state because it is bonded to two chloride ions. On the product's side of the equation, it has an oxidation state of zero because it is a pure element. Zinc has been reduced because the charge has been made less positive (+2 to 0) by the gain of electrons.
- Chlorine has a -1 oxidation state on both sides of the equation. It has been neither oxidized nor reduced.

In redox reactions, you can't have one element oxidized without another element having been reduced. After all, the movement of electrons causes both oxidation and reduction, so the total number of electrons removed from one thing through oxidation has to be the same as the number of electrons added to another through reduction. Because elements that gain electrons have pulled them away from the elements that have been oxidized, they are called *oxidizing agents*. Elements that have lost electrons have given them to elements that are reduced, so they are called *reducing agents*. In the previous example, sodium is the reducing agent (it caused zinc to be reduced) and  $\text{ZnCl}_2$  is the oxidizing agent (it caused sodium to be oxidized).

Because aluminum is oxidized in this reaction, the oxidation half-reaction is the following:



The half-reaction for the reduction of manganese is the following:



## Step 2

In each half-reaction, balance the elements that are oxidized or reduced. Next, balance any elements other than oxygen or hydrogen.

For the oxidation half-reaction, you balance the aluminum:



Because the reduction half-reaction is already balanced, you don't need to do anything with it.

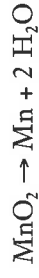
## Step 3

Balance the oxygen atoms by adding  $\text{H}_2\text{O}$  to the half-reactions when necessary.

For the oxidation half-reaction, you need to add three water molecules to the reactant side of the equation:



For the reduction half-reaction, you add two water molecules to the product side of the equation:



### THE MOLE SAYS

You add water to these equations because many redox reactions take place in water. Even for reactions that don't take place in water, the water molecules that you add in this step will eventually cancel each other out.

## Step 8

Cancel out any terms that are present in equal amounts on both sides of the resulting equation.

This leaves you with the following:

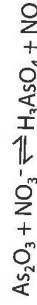


This is the correct answer!



### YOU'VE GOT PROBLEMS

Problem 3: Balance the following redox reaction:



## Voltaic Cells

So who uses electrochemistry, anyway? You do! One of the main uses of electrochemistry is in the batteries you use to power your MP3 player, pacemaker, wristwatch, and laser pointer. Someday soon, your car might even run on battery power! Because batteries are so important, let's learn more about them.

### Introduction to Voltaic Cells

As it turns out, another fancy word for *battery* is *voltaic cell* (or galvanic cell, if you want to be *really* fancy). The following figure shows an example of a voltaic cell.

Before you can get down to the nuts and bolts of how voltaic cells work, you need to understand some of the background information about them:

- The pieces of metal that are dipped into the solution in this diagram (the gray-shaded rectangles) are called electrodes. Electrodes are connected to one another by a wire on one side and through the solution on the other side.
- The electrode at which oxidation occurs is called the anode; the electrode at which reduction occurs is called the cathode. In this diagram, zinc is the anode and copper is the cathode.

One of the most important factors when considering how batteries work is their voltage. Voltage is a measure of how forcefully electrons are moved from one place to another. Voltage is defined as the amount of energy given off by a spontaneous electrochemical process or the amount of energy needed for a nonspontaneous redox reaction to occur. Wouldn't it be useful to figure out how to calculate the voltage of a battery?

You bet it would! To calculate the total standard cell potential, you use the following equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$$



#### THE MOLE SAYS

The little ° above the cell potentials in this equation indicates that the cell is running under standard conditions. Standard conditions, in redox reactions, mean that the concentrations of the reactants and products are both exactly 1 M for solutions and 1 atm for gases.

To find the potential of a cell, you need to add the potentials of the reactions that take place at the anode and cathode half-cells. Of course, this requires that you know what the half-cell potentials are.

Fortunately, nice chemists have already made big tables of half-cell potentials. Let's take a look at some standard reduction potentials.

Standard reduction potential (V)	Reduction half-reaction
2.87	$\text{F}_{(\text{g})} + 2 \text{e}^- \rightarrow 2 \text{F}^-_{(\text{aq})}$
1.99	$\text{Ag}^{+2}_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}^{+}_{(\text{aq})}$
1.82	$\text{Co}^{+3}_{(\text{aq})} + \text{e}^- \rightarrow \text{Co}^{+2}_{(\text{aq})}$
0.80	$\text{Ag}^{+}_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$
0.77	$\text{Fe}^{+3}_{(\text{aq})} + \text{e}^- \rightarrow \text{Fe}^{+2}_{(\text{aq})}$
0.52	$\text{Cu}^{+}_{(\text{aq})} + \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$
0.34	$\text{Cu}^{+2}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$
0.00	$\text{H}^{+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})}$
-0.28	$\text{Ni}^{+2}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Ni}_{(\text{s})}$
-0.44	$\text{Fe}^{+2}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Fe}_{(\text{s})}$
-0.76	$\text{Zn}^{+2}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Zn}_{(\text{s})}$
-1.66	$\text{Al}^{+3}_{(\text{aq})} + 3 \text{e}^- \rightarrow \text{Al}_{(\text{s})}$
-2.71	$\text{Na}^{+}_{(\text{aq})} + \text{e}^- \rightarrow \text{Na}_{(\text{s})}$



### CHEMISTRIVIA

Walther Nernst and Svante Arrhenius (of the eponymous equation) knew each other at university, and apparently didn't get along well. This dislike ran so deeply that Arrhenius blocked Nernst, an accomplished chemist, from winning the Nobel Prize for 16 years.

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

In this equation,  $E$  is the cell potential,  $E^\circ$  is the standard cell potential of the sort you calculated in the previous section,  $n$  is the number of electrons transferred in the reaction, and  $Q$  is the reaction quotient.



### THE MOLE SAYS

The reaction quotient for the generic process  $aA + bB \rightleftharpoons cC + dD$  is the following:

$$Q = \frac{[C_0]^c [D_0]^d}{[A_0]^a [B_0]^b}$$

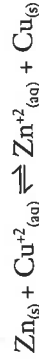
$C_0$  is the initial molarity of  $C$ ,  $D_0$  is the initial molarity of  $D$ , and so forth. For gaseous equilibria, partial pressures are used in lieu of molarities.

**Example:** For the cell  $Zn|Zn^{+2}||Cu^{+2}|Cu$ , what is the cell potential if the concentration of  $Zn^{+2}$  is 2.5 M and the concentration of  $Cu^{+2}$  is 0.75 M?

**Solution:** In the previous section, you found that  $E^\circ_{\text{cell}}$  for this process was 1.10 V. However, before using the Nernst equation, it's necessary to figure out what values you should use for all the variables.

For this process,  $n = 2$  because two electrons are transferred from  $Zn$  to  $Cu^{+2}$  in the cell.

To find the reaction quotient, you need to write the equation for the entire process and use it to find the reaction quotient:



$$Q = \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$$

As you learned in Chapter 19, you don't need to include solids in your equilibrium expressions because they don't have any concentration values that fit nicely into these equations

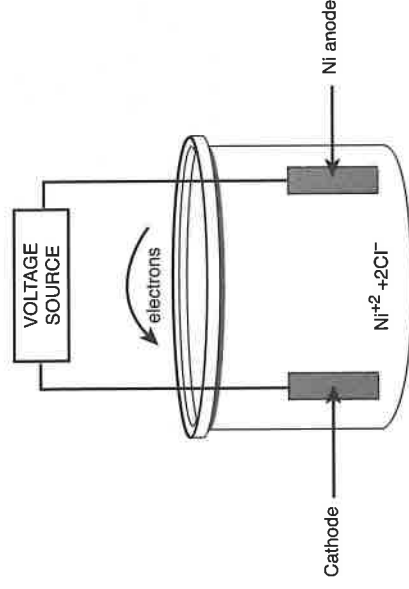


Figure 21.2: An electrochemical cell for plating nickel onto another metal.

In this electrochemical cell, the following process takes place.

1.  $\text{NiCl}_2$  dissolves to form  $\text{Ni}^{+2}$  and 2  $\text{Cl}^-$  ions.
2. When the cell is turned on,  $\text{Ni}^{+2}$  ions move toward the cathode and  $\text{Cl}^-$  ions flow toward the anode.
3. At the cathode (which is typically the item to be plated), the  $\text{Ni}^{+2}$  ions are reduced to form a thin layer of nickel.
4. Meanwhile, the nickel anode is oxidized, generating more  $\text{Ni}^{+2}$  ions to replace those that were plated on the cheap jewelry at the cathode.

During this process, the anode eventually disappears, having been electroplated onto the cathode.

### The Least You Need to Know

- The oxidation state of an element is equal to the amount of charge it can be considered to have in a compound.
- Oxidation occurs when an element loses electrons; reduction occurs when an element gains electrons.
- Redox reactions occur whenever a chemical change is accompanied by a change in the oxidation states of the elements present.

# Transition Metals and Coordination Compounds

Chapter

# 22

## In This Chapter

- What's a transition metal?
- The birth of a coordination compound
- Coordination compound nomenclature
- Our friends, the chelates

Up to this point, we've talked mostly about main block elements—our friends in the s- and p-blocks of the periodic table. As you might have guessed, however, these are not the only elements in the periodic table. In fact, there's a big bunch of elements called transition metals that we haven't paid much attention to just yet.

And why is that? Well, it turns out that, although main block elements are pretty straightforward in their chemistry, transition elements tend to cause trouble by doing some weird and interesting chemistry. However, after the last 21 chapters, I think you're probably ready to learn a little more about them. So, without further ado ....

## What's a Transition Metal?

Transition metals consist of the elements in the d- and f-blocks of the periodic table. When people say "transition metal," however, they almost certainly have in mind the elements in groups 3–12; f-block elements are usually referred to as either lanthanides or actinides (whichever is appropriate).

Because the transition metals are so important, let's talk about their properties in a little more detail than we did back in Chapter 4.



#### THE MOLE SAYS

Hydrates are compounds that have water molecules loosely attached to them. Many transition metals form hydrates, such as copper (II) sulfate and cobalt (II) chloride, both of which are brilliantly colored. The water molecules in hydrates can be removed by heating a hydrate (a process known as “dehydration”) and then can be rehydrated again by adding water.

## Coordination Compounds—Transition Metals in Action

In Chapter 20, you learned about acids and bases. Recall the Lewis definition of acids and bases: acids are compounds that accept electron pairs, and bases are compounds that donate electron pairs.

As it turns out, transition metal ions are usually really good Lewis acids. As a result, if chemical species that have electron pairs to donate happen to wander by, they usually donate those electrons to the transition metal ions.

These polar covalent compounds or ions that donate electron pairs to metal ions are called *ligands*. After these ligands have stuck themselves to a transition metal ion, the resulting chemical is called a *complex ion*. Common ligands include ammonia, water, halogen ions, and the cyanide ion. Ligands that donate one pair of electrons at a time are called monodentate ligands, whereas those that donate more than one pair of electrons are called polydentate ligands or chelating agents.



#### DEFINITION

**Ligands** are polar covalent molecules or ions that donate electron pairs to transition metal ions. The resulting combination of ligand and ion is called a **complex ion**.

Let's take a look at how complex ions are formed when ligands stick to transition metal ions.

### The Birth of a Coordination Compound

Imagine that you have a copper (II) ion in solution. With a formula of  $\text{Cu}^{2+}$ , copper is as happy as a clam, just floating around and having a good time.

## Naming Coordination Compounds

Remembering back to when we named ionic compounds, I said that ionic compounds have two-word names. The first word is the name of the cation, and the second is the name of the anion. This is still true for coordination compounds.

What's not true, however, is that the names of these ions are necessarily very simple. Consider how you go about naming complex ions. Here are some rules, to give you a hand:

- In the name of the complex ion, the names of the ligands are named in alphabetical order, followed by the name of the metal. If there's more than one ligand present, use a prefix (di-, tri-, tetra-, and so on).



### THE MOLE SAYS

If the ligand in a coordination compound has a prefix in it (for example, the ethylenediamine ligand, usually abbreviated as "en"), put it in parentheses and write the prefix as "bis-" for two, "tris-" for three, "tetrakis-" for four, and so forth.

- If a ligand is an anion, it ends with the letter *o*. If it is not, it's just the name of the neutral molecule. About the only interesting ligand names you might not know are those of the  $\text{NH}_3$  ligand (ammine—spelled differently from the "amines" you read about in Chapter 23) and the  $\text{H}_2\text{O}$  ligand (aqua).
- If the complex ion is an anion, it ends in "-ate." If not, it has no special ending.
- The oxidation number of the metal ion is always given after its name in the complex ion.

Let's take a look at how this works in naming  $\text{K}[\text{Co}(\text{OH})_4]$ . The first name of this compound is potassium and the second name is tetrahydroxocobaltate (III), giving you the overall name of potassium tetrahydroxocobaltate (III).



### YOU'VE GOT PROBLEMS

Problem 1: Name the following coordination compounds:

- $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$
- $\text{K}_4[\text{NiCl}_4]$
- $\text{Li}[\text{Al}(\text{CN})_4]$

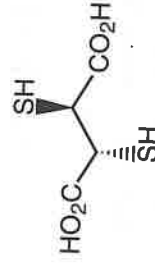


Figure 22.3: DMSA, a common heavy metal poisoning treatment.



#### BAD REACTIONS

In addition to legitimate uses such as the treatment of heavy metal poisoning, chelating agents such as ethylenediaminetetraacetic acid (EDTA) are sometimes used in holistic medicine for the treatment of atherosclerosis, despite a complete lack of evidence that it works.

Chelates are also naturally produced by living things. Heme, which is the part of hemoglobin responsible for the oxygenation of our blood, consists of a porphyrin chelate surrounding an iron (II) ion. You can see from the following diagram how the iron is held tightly in place by the four nitrogen atoms present on the porphyrin ring:

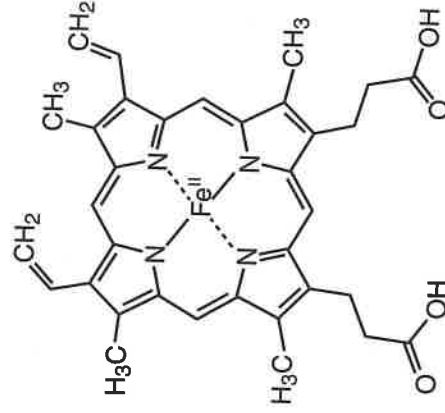


Figure 22.4: Heme, which is responsible for carrying oxygen in our blood.

# Organic Chemistry

## Chapter 23

### In This Chapter

- Hydrocarbons
- Isomerism
- Functional groups
- Basic organic reactions







Organic chemistry is a lot of fun. When you understand how organic molecules react with one another, you truly get a feel for how rich and exciting the field of chemistry really is. The first time I took organic chemistry, I was hooked!

Unfortunately, organic chemistry is much too big a subject to discuss in any detail in a general chemistry course. As a result, students usually don't understand why they have to learn it or how it fits with the rest of chemistry. Because I realize that this is a problem with how organic chemistry is taught in a first-year course, I focus my attention on topics you're likely to see on a test. It's my hope that you'll decide to take a course devoted solely to organic chemistry so that you can see how cool it really is. Plus, it's cool in combination with *The Complete Idiot's Guide to Organic Chemistry* (available at fine booksellers everywhere).

So sit back and relax as we take a whirlwind tour through organic chemistry.

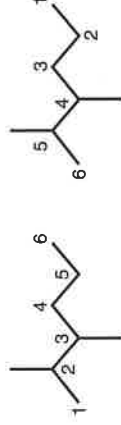
### What Is Organic Chemistry?

After the big buildup I just gave organic chemistry, you might be wondering what it is. Organic chemistry is the study of carbon-containing molecules. Most compounds that contain carbon are referred to as organic molecules; the only common carbon-containing inorganic compounds are CO, CO<sub>2</sub>, and the carbonates.

Number of carbon atoms	Name	Formula	Structure
1	methane	CH <sub>4</sub>	$\begin{array}{c} \text{H} \\   \\ \text{H} - \text{C} - \text{H} \\   \\ \text{H} \end{array}$
2	ethane	C <sub>2</sub> H <sub>6</sub>	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H} - \text{C} - \text{C} - \text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
3	propane	C <sub>3</sub> H <sub>8</sub>	
4	butane	C <sub>4</sub> H <sub>10</sub>	
5	pentane	C <sub>5</sub> H <sub>12</sub>	
6	hexane	C <sub>6</sub> H <sub>14</sub>	
7	heptane	C <sub>7</sub> H <sub>16</sub>	
8	octane	C <sub>8</sub> H <sub>18</sub>	

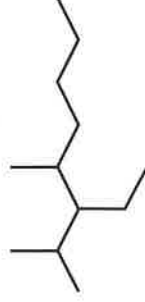
**Figure 23.1:** *The first eight straight-chain hydrocarbons. Make sure you memorize the names of these compounds—you'll need them later!*

In Figure 23.1, all the atoms for methane and ethane are shown, but for propane through octane, only straight lines are drawn. This is a common shorthand method for showing the structure of organic molecules. It's assumed that each of the intersections between lines corresponds to carbon atoms, as do the ends of each line. Hydrogen atoms are added to this structure so that all carbon atoms have a total of four bonds. To completely draw out pentane, follow the steps in Figure 23.2.



**Figure 23.4:** The numbering on the left is correct because the methyl groups are located on the 2 and 3 positions rather than the 4 and 5 on the right.

- If there's more than one of a substituent, use the prefix "di-" to indicate that there are two, "tri-" for three, "tetra-" for four, and so on. Before the prefixes, indicate which carbon each group is stuck to. In the example, the molecule is referred to as "2,3-dimethylhexane" because one methyl group is on the second carbon and one is on the third. Take care to include a hyphen between the numbers and the name.
- If there's more than one type of substituent, write them in alphabetical order, regardless of their position on the chain or prefixes. For example, the molecule in Figure 23.5 is called 3-ethyl-2,4-dimethyloctane.



**Figure 23.5:** 3-ethyl-2,4-dimethyloctane.



#### YOU'VE GOT PROBLEMS

Problem 1: Draw the structures of the following compounds:

- 4-ethyl-2-methylhexane
- 2-chloro-3-methylheptane
- 1,2,2-trichloroethane

## Alkenes and Alkynes

Alkenes and alkynes are both unsaturated hydrocarbons, which means that there's at least one C-C multiple bond. Alkenes have at least one C-C double bond, and alkynes have at least one C-C triple bond.

cycloalkyne. These molecules are named in the same way that straight-chain hydrocarbons are named, except that the carbon atoms in the ring are numbered such that the substituents have the smallest possible numbers. An example of a cyclic cycloalkane is 1,2-diethylcyclopentane.

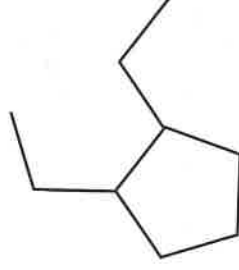


Figure 23.8: 1,2-diethylcyclopentane.



#### YOU'VE GOT PROBLEMS

Problem 3: Draw the following organic compounds:

- a) 1-ethyl-3-methylcyclohexane
- b) 1,2,3-trimethylcyclopropane

Though cyclic molecules with three atoms can be formed, these molecules aren't stable. Recall from Chapter 7 that  $sp^3$  hybridized atoms prefer to have a  $109.5^\circ$  bond angle. However, in cyclopropane, the bond angle is forced to be a small  $60^\circ$ , which puts a lot of strain on the ring. This ring strain is called, straightforwardly enough, "ring strain." Generally, five- and six-membered rings have the least ring strain and are most commonly formed.



#### YOU'VE GOT PROBLEMS

Problem 4: Explain why cyclopropane is even less stable than cyclopropane, using your knowledge of bond hybridization.

## Aromatic Hydrocarbons

Aromatic hydrocarbons are cyclic molecules that are drawn with alternating carbon-carbon single and double bonds. The rock star of the aromatic hydrocarbon world is benzene.

## Constitutional Isomerism

Constitutional isomers are molecules that have the same formulas but differ in the order in which the atoms are connected to each other. An example of constitutional isomerism is shown here in two molecules that both have the formula  $C_4H_{10}$ :

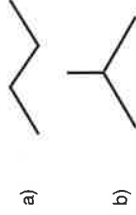


Figure 23.11: Constitutional isomers a) butane and b) 2-methylpropane.

## Stereoisomerism

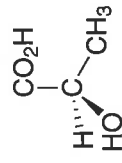
*Stereoisomers* are molecules in which the atoms are bonded in the same order, but with different spatial orientations. To imagine what a stereoisomer looks like, hold your hands in front of you. Though each has four fingers and a thumb connected to your palm, your hands are different from each other, in that they can't fit into the same glove.



### DEFINITION

**Stereoisomers** are molecules in which the atoms are bonded in the same order, but with different “handedness” orientations. Molecules that have stereoisomers are said to be **chiral**.

A good rule of thumb is that any organic molecule in which four different things are stuck to any of the carbon atoms is *chiral* (for example, it has the “handedness” relationship between stereoisomers). One example of a molecule like this is *R*-lactic acid:



*R* - lactic acid

Figure 23.12: *R*-lactic acid, a chiral molecule.

Functional group	General Formula	Example	Name
alkyl halide	R-X	CH <sub>3</sub> Br	bromomethane (methyl bromide)
alcohol	R-OH	CH <sub>3</sub> OH	methanol
ether	R-O-R' (R groups not necessarily the same)		diethyl ether
aldehyde			ethanal (acetaldehyde)
ketone			propanone (acetone, dimethyl ketone)
carboxylic acid			ethanoic acid (acetic acid)
ester			ethyl ethanoate (ethyl acetate)
amine			triethylamine

Figure 23.14: The most common organic functional groups and their names.

## Organic Reactions

Now that you're familiar with organic chemicals, it's time to learn about their reactions. The most comprehensive organic chemistry manual I own covers only the fundamentals of organic chemistry, and it's 1,495 pages long. Because I'm sure you don't want to read a 1,500-page chapter, the following is a *very* abbreviated list of organic reactions.

Likewise, when water reacts with alkenes or alkynes, this forms alcohols. As with the preceding reaction, the  $-OH$  group always winds up on the carbon atom, which has fewer hydrogen atoms bonded to it.

## Free-Radical Substitution Reactions

Alkyl halides can be formed when alkanes react with halogens in the presence of light. This process takes place through a free radical process. Free radicals are highly reactive atoms or groups of atoms with an unpaired electron.

Free-radical reactions typically take place in a three-step chain reaction. You can see how this works for the reaction of chlorine with ethane to form chloroethane, for which the overall reaction follows this equation:

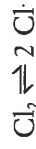
*light*



### Step 1: The Initiation Step

In the initiation step, the reactive species is generated when a halogen is broken apart with light:

*light*

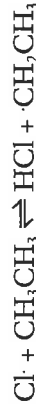


#### THE MOLE SAYS

That dot next to some of these chemicals isn't a typo! It represents the unpaired electron in a free radical and is responsible for their high reactivity.

### Step 2: The Propagation Step

The propagation step involves the chlorine radicals reacting with the alkane molecule to form alkane radicals. In turn, the alkane radicals can react with halogen molecules to form more alkane radicals. The propagation steps for this reaction are shown here:



## Condensation Reactions

In condensation reactions, two molecules combine with one another in a way that results in the formation of water. One example of a condensation reaction occurs when two molecules of methanol combine with one another to form dimethyl ether and water.



Figure 23.20: Two molecules of methanol condense to form dimethyl ether and water.

## Polymerization Reactions

Earlier in this chapter, I mentioned that carbon was good at forming long chains. One of the ways this process occurs is by polymerization.

In a polymerization reaction, small molecules called monomers link up with one another to form much longer chains of molecules called polymers. Most of the plastics you're familiar with are polymers such as Teflon (polytetrafluoroethane), polyethylene, and polystyrene.



### CHEMISTRIVIA

Teflon (found on nonstick cookware, among other things) was discovered accidentally when DuPont scientists, working on new CFC refrigerants, found that they couldn't get the tetrafluoroethylene in a pressurized tank to come out. When the scientists sawed the tanks open, they found that the gas had polymerized and formed an almost completely unreactive solid.

The free radical reaction that forms polyethylene from ethylene monomers is shown in Figure 23.21.

# Biochemistry

## Chapter 24

### In This Chapter

- Amino acids and proteins
- Enzymes
- Carbohydrates
- Fats and oils
- Nucleic acids

By now, you're probably comfortable with doing a chemical reaction in a beaker. If you're feeling really wacky, you might even do a reaction in a flask or a test tube.

However, if you're somebody who likes to live on the edge, you might want to consider doing reactions inside a living body. Yes, beakers and flasks aren't the only place chemistry occurs—it also happens within every living organism. Straightforwardly enough, this “biological chemistry” is called biochemistry.

Again, as with organic chemistry, you're going to get the quickest of glimpses into the world of biochemistry. Hopefully this will whet your appetite for more!

### What Is Biochemistry?

*Biochemistry* is the study of chemistry as it occurs in living organisms. From the photosynthesis that takes place in plants to the digestion of the burrito you had for lunch yesterday, biochemistry covers every chemical change that happens inside your (or anything else's) skin. As you might imagine, there's a lot of chemistry going on in there.



### DEFINITION

**Amino acids** are small molecules that are the building blocks of proteins. Their name derives from the fact that these compounds contain both an amino group and a carboxylic acid group.

Think back to Chapter 23, and you can see how amino acids get their name. These molecules contain both an amino group (the  $-\text{NH}_2$  group in the structure) and a carboxylic acid group (the  $-\text{COOH}$  group). The R- group can be a wide variety of things—the identity of this group distinguishes the amino acids from one another. The naturally occurring amino acids are shown in Figure 24.2:

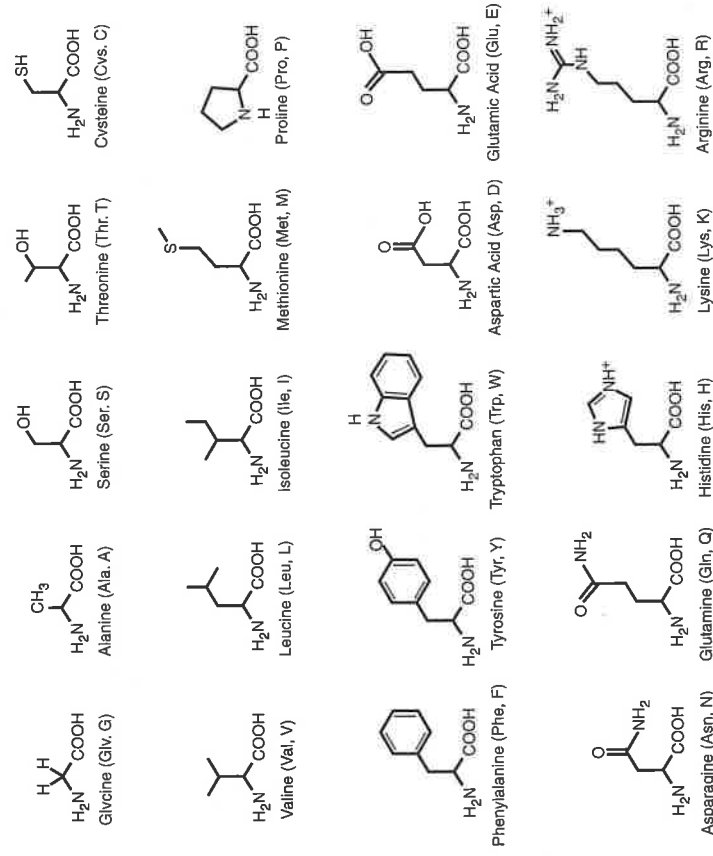


Figure 24.2: The naturally occurring amino acids.

## Properties of Amino Acids

Because the amino acids are so important in biochemistry, it's good to learn more about them before charging into the realm of proteins and such. Take a look at some of the properties of amino acids.

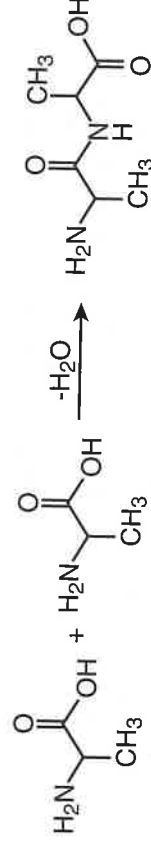


Figure 24.5: This reaction shows the combination of two alanine molecules to form the alanylalanine dipeptide.



#### THE MOLE SAYS

When molecules such as the dipeptide alanylalanine combine with other amino acids, the peptide chain grows into a longer polypeptide. Eventually, the chain grows into a molecule with a molecular weight higher than 10,000 atomic mass units—this is the cutoff point between a polypeptide and a protein.

## Proteins

Because you've been so good about learning biochemistry, we can have a storytime break. Sit back, relax, and enjoy the following tale.

Once upon a time, there was an amino acid that formed a peptide bond with another amino acid. The resulting molecule was called a dipeptide, and this dipeptide bonded with another amino acid to form a polypeptide. This polypeptide, in turn, combined with additional amino acids until the chain grew very long and a protein was born.

When the protein got older, he told his buddies that he was going to go out into the great wide world. His buddies, however, informed him that he needed to have a name. He thought and thought, and eventually decided to name himself after the amino acids that comprised his primary structure. After examining the amino acids in his chain, he decided to call himself ser-thr-asp-pro-val- (*Editor's note: I have decided to cut this short, because the primary structure of this protein goes on another 43 pages*). As you can see, the primary structure of a protein is just a list of the amino acids, as you move from the amino end of the protein to the carboxylic acid end.



#### CHEMISTRIVIA

Even a small change in the primary structure of a protein can cause a big change in the protein's function. For example, sickle-cell anemia results from a single mistake in the primary structure of hemoglobin.

intertwined with one another. This quaternary protein structure, in which two protein chains cluster together, made both of them very happy.

Unfortunately, all was not well in the land of the protein. When Dr. Meanie, a scientist working for the World Health Organization, realized that this happy protein was the cause of a disease that caused insanity in goats, he decided to destroy it. Because he knew that proteins could be denatured (that is, have their function destroyed by unraveling) through either heating or pH change, he decided to kill our protein friend by developing a medicine that would selectively protonate some of its active sites. Though the goat world was thankful, his friends sorely missed him. The end.

## Enzymes

In our bodies, we have a lot of chemical reactions that need to take place to keep us alive. These reactions all happen unbelievably slowly under normal conditions, so they need a catalyst to help them move at a rate that enables us to live. These biological proteins that catalyze biochemical reactions are called *enzymes*.



### DEFINITION

An **enzyme** is a protein that catalyzes biochemical reactions.

How does a catalyst work? I'm glad you asked! Catalysts have active sites within their structure where certain molecules undergo the required reaction. Because only one reaction can be catalyzed per site, this model is called the lock-and-key model of enzyme activity—just as a lock can hold only one key, an enzyme's active site can accommodate only one chemical reaction.

Interestingly, your understanding of enzymes can help you understand some of the ways in which biological systems break down. For example, lead and mercury poisoning can be caused when the metal atoms inhibit the active sites on various enzymes, stopping reactions from occurring. Similarly, very high fevers can be fatal because they cause the enzyme structure to denature, making it useless as a catalyst.

## Carbohydrates

If you have a sweet tooth, you've probably eaten your share of sugar. As it turns out, this sugar that you've been so happily consuming is one of a large class of compounds called carbohydrates, which are molecules that have distinctive chemical structures. The best-known carbohydrates for most people are glucose and fructose.

Glucose and fructose are both simple sugars, or monosaccharides. However, they can join with each other in a dehydration reaction to form disaccharides such as sucrose, or form even longer chains called polysaccharides.



#### THE MOLE SAYS

Sucrose is a disaccharide formed from the combination of glucose and fructose. Other disaccharides include maltose (glucose + glucose) and lactose (galactose + glucose).

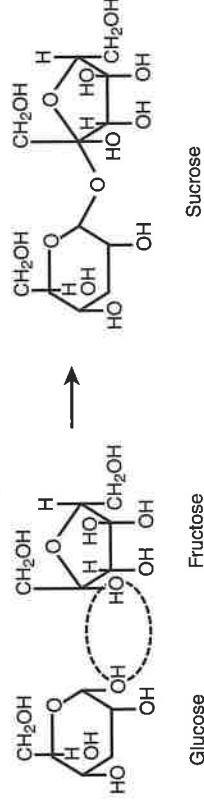
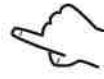


Figure 24.9: The formation of sucrose from glucose and fructose.

## Polysaccharides

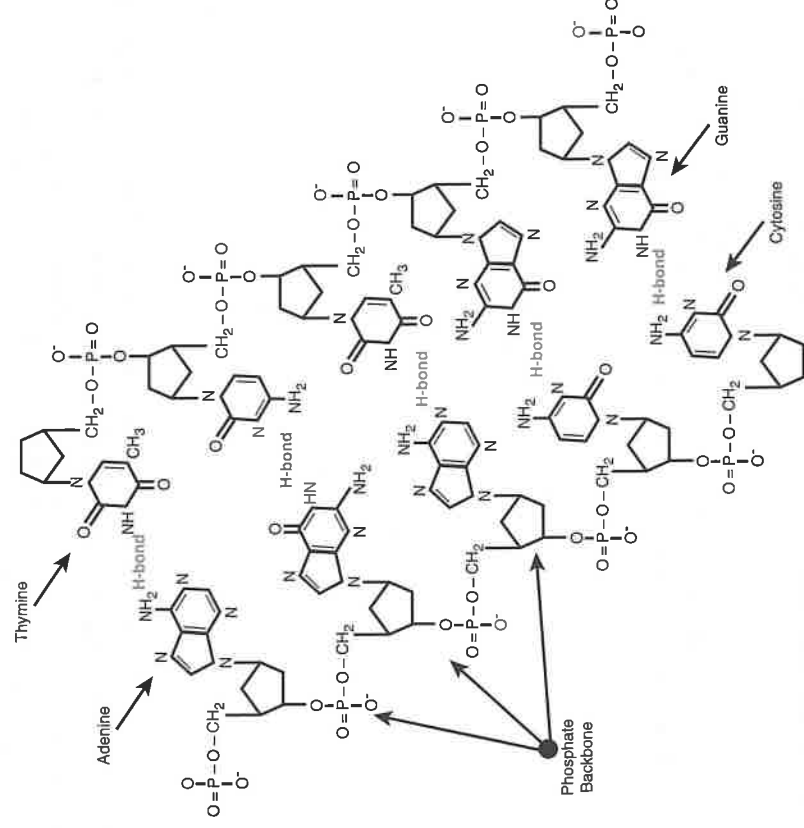
Polysaccharides are carbohydrates formed when monosaccharide units combine with one another. Some of these large carbohydrates include the following:

- Starch is a type of polysaccharide formed in plants. The carbohydrates in potatoes, rice, and wheat are examples of starches.
- Glycogen is a polysaccharide formed in the body and stored in the liver as a source of glucose in the blood.
- Cellulose is a structural material made in plants. Unlike starch, humans can't digest cellulose, though many animals and bacteria can.



#### CHEMISTRIVIA

You probably know cellulose better as the dietary fiber that you consume each day in fruits and vegetables for good colon health.



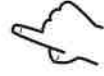
**Figure 24.11:** The basic structure of DNA consists of phosphate groups, deoxyribose sugars, and nitrogen-containing bases.



#### THE MOLE SAYS

The structures of DNA and RNA differ in two main ways, in addition to the fact that DNA has two strands and RNA has one. First, the sugar in DNA is deoxyribose, whereas in RNA it is ribose. Additionally, the thymine that is present in DNA is replaced with uracil in RNA.

DNA is a double-stranded nucleic acid, whereas RNA generally has one strand. As you can see from Figure 24.11, the two strands of DNA are held together by our old friend hydrogen bonds (refer to Chapter 10). This relatively weak intermolecular force enables the strands to stay together most of the time but “unzip” into individual strands when needed for replication. RNA also interacts with bases using hydrogen bonds when coding for proteins or performing other tasks in the cell.

**CHEMISTRIVIA**

Two-time Nobel Laureate Linus Pauling was one of the people in the race to find the secondary structure of DNA. His model involved a triple helix, not the double-helix model that James Watson and Francis Crick devised in the 1950s.

**The Least You Need to Know**

- Biochemistry is the study of chemistry as it occurs in living organisms.
- Amino acids are the basic building blocks of proteins.
- Proteins have a primary structure that corresponds to the order of amino acids, a secondary structure that corresponds to whether it folds into a helix or a sheet, a tertiary structure that corresponds to how this helix and/or sheet twists, and a quaternary structure that corresponds to how it interacts with other proteins.
- Enzymes are biological catalysts and work by the lock-and-key mechanism.
- Polysaccharides, fats, and oils are different molecules that are often found in biological systems.
- Nucleic acids are responsible for encoding genetic information and protein synthesis in a cell.

# Nuclear Chemistry

## Chapter 25

### In This Chapter

- Commonly used terms
- Types of radioactive decay
- Half-lives
- Binding energy
- Fission
- Fusion

Nuclear reactions have an interesting history. In the beginning of the nuclear age, nuclear reactions were seen as a force for good. Not only did they end World War II, but they were set to make electricity so cheap that it wouldn't even be metered. However, nowadays only “rogue states” are trying to get their hands on nuclear weapons, and “nuclear reactor” is synonymous with “meltdown” in many people's minds. Depending on how you look at it, nuclear reactions are either very good or very bad.

So is nuclear energy a good thing, or will it end up killing us all? I don't know, and I'm certainly not going to take sides in this issue because I don't want the hate mail I'd get as a result. However, I do hope that learning a little more about nuclear reactions and how they work enables you to make an informed decision one way or the other.

### What Are Nuclear Reactions?

Nuclear reactions are reactions that involve the nucleus of an atom. Many types of nuclear reactions take place, but one thing they all have in common is that the atom itself is changed, not just the manner in which it combines with other atoms. As you see in this chapter, each type of nuclear reaction has its own characteristics.

stable isotopes is about 1:1 (as is the case in calcium-40, which has 20 protons and 20 neutrons). For elements with higher atomic numbers, this ratio gradually rises, as seen in bismuth-209, which has 129 neutrons and 83 protons (giving it a 1.5:1 neutron/proton ratio).

3. Nuclides containing “magic numbers” of protons or neutrons appear more stable than other nuclides. These magic numbers are 2, 8, 20, 50, 82, and 126. For example, there are more stable nuclides with 20 protons than stable nuclides with either 19 or 21 protons. This is generally understood to be the result of the filling of nuclear energy levels, similar in concept to the octet rule in filling orbitals with electrons.



#### CHEMISTRIVIA

It is thought that there might be a “magic island” of superheavy elements that might have much greater-than-able stabilities. Though elements with atomic numbers greater than 107 have extremely short half-lives (on the order of milliseconds), some scientists think that there might be some relatively stable nuclides still out there, waiting to be discovered.

4. Nuclides with even numbers of both protons and neutrons are more stable than those with odd numbers of protons and neutrons. This phenomenon is understood based on theories of how protons and neutrons interact in atomic nuclei.

These rules have exceptions, which isn't surprising, given that they are based on an esoteric theory about how the strong nuclear force works. However, if you're not sure whether something will be radioactive, these guidelines are more accurate than making random guesses!

## Types of Radioactive Decay

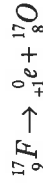
Atoms can undergo radioactive decay in many ways to become more stable. We discuss the possible methods of radioactive decay, as well as offer suggestions so you can make a rough prediction of what type of decay a certain nuclide will undergo.

### Alpha Decay ( $\alpha$ )

Alpha particles, depicted by the Greek letter  $\alpha$ , consist of helium nuclei and have the formula  ${}^4_2\text{He}^{+2}$ . Isotopes that give off alpha particles are said to have undergone alpha decay.

## Positron Emission

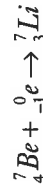
Positrons are the antiparticles of electrons and have the symbol  ${}^0_{+1}e$ . Positron emission results in the conversion of a proton to a neutron, decreasing the atomic number of the nuclide by one but leaving the atomic mass unchanged.



Positron emission most often occurs when an element has a small neutron-to-proton ratio. In the preceding example, the neutron-to-proton ratio of fluorine-17 is 0.89:1.

## Electron Capture

Electron capture occurs when an electron in an inner orbital is pulled into the nucleus, converting a proton into a neutron. As in positron emission, this most often occurs in nuclides where the neutron-to-proton ratio is too small. An example of this is shown here.



### YOU'VE GOT PROBLEMS

Problem 1: Write the equations for the following decay processes:

- Silver-108 undergoes beta decay.
- Radon-216 undergoes alpha decay.

## Half-Lives

In Chapter 18, we discussed the concept of half-lives. To recap, the half-life of a reaction is the amount of time it takes for half of the reactant to be converted into products.

In nuclear reactions, the half-life of the reaction is the amount of time it takes for half of the radionuclide atoms to undergo radioactive decay. Fortunately for us, nuclear half-lives use the same rate laws as first-order chemical processes. As a result, the following equation determines the half-life of a nuclear reaction:

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$t_{1/2}$  is the half-life of the process, and  $k$  is its rate constant.



## YOU'VE GOT PROBLEMS

Problem 2:

- Determine the rate constant for the alpha decay of gadolinium-148, given that the half-life of this process is 74.6 years.
- If you started with 85.0 g of gadolinium-148, how many grams would remain after 675 years passed?

## Binding Energy—Relating Mass to Energy

Let's do some simple math. The mass of a proton is 1.00728 amu. The mass of a neutron is 1.00867 amu. If you have 92 protons and 146 neutrons in a nucleus of  $^{238}\text{U}$ , this nucleus should weigh (if you do the math) 239.94 amu.

There's just one small problem: the actual mass of the  $^{238}\text{U}$  nucleus is 238.03 amu. What happened to the other 1.31 amu?

As it turns out, the missing mass (called the *mass defect*) has been converted to energy. Albert Einstein said that mass and energy can be converted to one another using the equation  $E = mc^2$ , where  $E$  is energy (in J),  $m$  is mass (in kg), and  $c$  is the speed of light ( $3.00 \times 10^8$  m/s). In our example, the missing mass is in the form of energy that holds the nucleus together.



## DEFINITION

The **mass defect** of a nucleus is the difference in mass between the mass of the nucleus and the mass of its constituent protons and neutrons. The **binding energy** of a nucleus is the mass defect converted into energy.

So how strongly held is this, really? Well, for 1 mol of uranium, the *binding energy* is  $1.18 \times 10^{14}$  J, which, if you could capture it, could raise the temperature of 330 million kilograms of water by  $90^\circ\text{C}$ . That's a lot of energy!

## Nuclear Fission

Nuclear fission is one of the processes that enables us to generate large quantities of energy from nuclear processes. In a *fission reaction*, a heavy nucleus is hit with a neutron, which causes it to break apart. Because this releases some of the binding energy of this nucleus, this process gives off a lot of heat.

This process requires temperatures of approximately 40 million degrees to occur. Because temperatures of this magnitude are found only in stars and atomic bombs, fusion reactions are impractical as commercial energy sources at this time.

### The Least You Need to Know

- Radioactive decay occurs because some atomic nuclei are unstable.
- The main types of radiation are alpha decay, beta decay, gamma decay, positron emission, and electron capture.
- The amount of time it takes for half of a radioactive sample to decay is its half-life.
- The amount of mass that's converted to energy in a nucleus is called the mass defect. When converted to energy, this value is referred to as the binding energy.
- Fission occurs when a nucleus breaks apart to form smaller nuclei, whereas fusion occurs when smaller atoms join together to form a larger nucleus. Both processes give off a great deal of heat.

# Thermodynamics 101

Part

6

In my chemistry classes, I like to do demonstrations in which things explode. After all, who doesn't like to see something blow up?

Even if you have terrible lab skills, things don't just blow up for no reason. They blow up because energy, like anything else, behaves according to certain rules that take some getting used to. These rules are called thermodynamics.

In this last part of the book, you learn why some reactions occur spontaneously, whereas others don't happen at all. Of course, this involves learning fancy terms like *entropy*, *enthalpy*, and *free energy*, but you'll get the hang of it in no time!

# Cranking Up the Heat: Basic Thermodynamics

## Chapter 26

### In This Chapter

- Energy, heat, and temperature
- Enthalpies of formation
- Finding enthalpies of reaction using Hess's law
- Calorimetry

As we approach the end of this book, it's clear that we haven't spent much time discussing energy. Sure, I mentioned it a little bit back in Chapter 17 when I told you about energy diagrams, but we haven't really talked about what energy is or how it works.

Well, that's about to change. Pull out your calculators and get ready to crank up the heat.

### What Is Energy?

This seems like a simple question. After all, if you put your hands on a hot stove burner, you'd know from your flaming fingers that energy was transferred from the burner to your hands. However, having an intuitive feel of energy isn't the same thing as defining it.

*Energy* is defined as the capacity of something to do work or produce heat. For example, if I feed my son, Steve, 15 chocolate bars, I'll find out from the resulting hyperactive behavior that the chocolate contained a considerable quantity of energy.

You need to be concerned with two types of energy:

- *Kinetic energy* is the energy having to do with how fast something moves. For example, if my chocolate-filled son decided to roll a bowling ball down the stairs, the resulting destruction in my living room would make me realize that the moving bowling ball had introduced a lot of energy to my entertainment center.

that the temperature is  $25^{\circ}\text{C}$ . This might be true, but it doesn't actually answer the question you were asked.

The term *temperature* describes the amount of motion that the molecules or atoms in a material have. If these particles are moving quickly, the material has a high temperature. If the particles move slowly, the material has a low temperature.

*Heat*, on the other hand, describes the amount of energy that is transferred from one object to another. When you go outside on a hot day, you don't feel hot because the air molecules are moving quickly—you feel hot because these molecules are colliding with you and transferring some of their energy to your skin. Though this is a subtle difference, it will become important later.



#### DEFINITION

**Temperature** describes the motions of the particles in a material, and **heat** describes the amount of energy moved from one object to another during some process.

## Describing Energy Changes

Let's say that you have a closed can of beans sitting in the trunk of your car. It's a hot day, and the temperature inside your car is  $50^{\circ}\text{C}$ . Now imagine that you put this can of beans into a bucket of ice. It won't be any surprise to find that the energy of the beans transfers to the ice, causing it to melt.

In thermodynamic terms, you think of the can of beans as being the system and the ice as the surroundings. The *system* in thermodynamics refers to some object that we're interested in studying—in this case, we care a lot more about the energy in the can of beans than we do about the bucket of ice. The *surroundings*, on the other hand, are defined as anything other than the system. In this case, it refers to the bucket of ice, as well as the surrounding room, the country you live in, the solar system, and so forth. Because most of the surroundings aren't terribly important when studying what happens to the can of beans (I doubt that the Andromeda galaxy notices this phenomenon), a more functional definition of the surroundings in thermodynamics is “the thing that interacts most closely with the system.”



#### DEFINITION

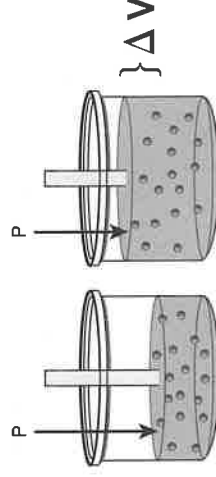
The **system** is the object that you're interested in studying, whereas the **surroundings** are the part of the universe with which the system exchanges energy.

## Energy Is a State Function

After reading the previous statement, you're probably asking yourself, "What the heck is a state function?" This means that the energy of a system depends on the conditions present in the material, such as the temperature, pressure, and quantity of the material. It doesn't matter where the material came from—the only thing that matters is its current condition.

## P-V Work

One type of work that's fairly common in chemical processes is work having to do with the expansion or contraction of gases. In an automobile, the expanding gases in the cylinders cause a piston to move, which ultimately causes the car to move forward. Figure 26.1 shows how a gas performs work in a piston:



**Figure 26.1:** *When the gas in a cylinder expands, the product of the change in volume ( $\Delta V$ ) and the outside pressure ( $P$ ) is equal to the amount of work performed.*

In this example, the gas in the cylinder performed work by pushing on a piston. When the piston is pushed outward, the difference between the initial and final volume of the piston is referred to by the term  $\Delta V$ . Because an external atmospheric pressure is exerted on the piston ( $P$ ), the amount of work the gas performs is:

$$w = -P\Delta V$$

The sign for work in this expression is negative because the gas is performing work on its environment, which transfers energy from the system to the environment.

Earlier, we defined the change in energy for a process as the following:

$$\Delta E = q + w$$



### DEFINITION

The enthalpy change for a chemical reaction is more commonly known by the term **heat of reaction** and has the symbol  $\Delta H_{\text{rxn}}$ . The enthalpy required for a chemical to be created from its elements is called the **heat of formation** and has the symbol  $\Delta H_f$ .

When the *heats of formation* for a series of chemical compounds are given, the symbol is usually given as  $\Delta H_f^\circ$ . The little  $^\circ$  after the  $\Delta H$  appears insignificant but means that the heat of formation given is for the form of the substance that's most stable at a pressure of 1 atm and 298 K (25 $^\circ$  C). The proper term for a heat of formation under these conditions is a standard heat of formation, because it's determined under the standard conditions for thermodynamics. Oddly, the standard temperature for thermodynamics is 25 $^\circ$  C, not the 0 $^\circ$  C that you learned for gas laws. Go figure.



### THE MOLE SAYS

The standard heats of formation for pure elements is said to be zero, as long as the elements are in their most stable form. For example, the standard heat of formation of  $\text{O}_2$  is zero, but the standard heat of formation of  $\text{O}_3$  is higher because it's less stable than  $\text{O}_2$  under standard conditions.

To understand all this stuff, let's do an example and make it clearer.

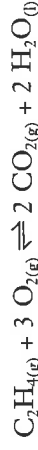
**Example:** Find the heat of combustion of ethene, given the following information.

$$\Delta H_f^\circ(\text{C}_2\text{H}_{4(g)}) = +52.3 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{CO}_{2(g)}) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}_{(l)}) = -285.8 \text{ kJ/mol}$$

**Solution:** Before you can do anything, you must write a balanced equation for the combustion of ethene:



The heat of combustion for this process is equal to the sums of the heats of formation for the products minus the sums of the heats of formation for the reactants. Chemists usually like to write this in the form of the following equation:

$$\Delta H_{\text{rxn}} = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

## Hess's Law

Sometimes the reactants in a chemical process need to undergo several changes to become products. For these multistep processes, the sum of the enthalpy changes for all the steps is equal to the overall enthalpy change for the process. This is known as Hess's law.

What does this mean? Well, let's say that you decide to go hiking up a mountain. On the first day, your elevation change was 2,000 m, while on the second day of your hike, the elevation change was -1,000 m. If somebody asked you to find your overall elevation change, you'd say that it was +1,000 m, because the sum of the altitude changes is equal to your overall altitude change. Hess's law says the same thing, except that it's talking about reactions instead of hikes and  $\Delta H$  instead of altitude.

Maybe doing a chemical example will help.

**Example:** Determine the enthalpy of formation of  $N_2O_3$ , which occurs via the reaction  $2 N_2 + 5 O_2 \rightleftharpoons 2 N_2O_3$ .

Now, I was too lazy to look up a table of heats of formation. Fortunately, you have to do this using the following standard heats of reaction:



You might wonder why it's fortunate that we have this information. After all, what do all these reactions have to do with the one we're interested in?

I'm glad you asked! By combining the preceding equations, you come up with a whole new equation that describes the process you're interested in. The only rules you need to follow are the following:

- If you reverse a reaction, the sign of the standard heat of reaction is reversed. For example, the following process has a  $\Delta H^\circ_{rxn} = +114.0 \text{ kJ}$ :



- If you need to perform a reaction more than once, the heat of reaction is multiplied by the number of times you do the reaction. For example, if you do the following reaction twice, the heat of reaction will be  $2 \times -114 \text{ kJ} = -228 \text{ kJ}$ :

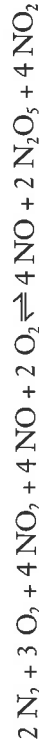


By multiplying this equation by 2, you cancel out the  $\text{NO}_2$  on the reactant side and the  $\text{NO}$  on the product side of the previous reaction.



## Step 5

Add the equations from step 3 and step 4 together. This gives you the following:



Cancelling out and combining terms, you find the following, which is what you wanted:



or



Now all you need to do is add the heats of reaction for the reactions in step 3 and 4 to find the total standard heat of formation for this process:

$$\Delta H^\circ_f = +252 \text{ kJ} - 228 \text{ kJ} = 24 \text{ kJ}$$



### THE MOLE SAYS

Hess's law problems take a lot of time and practice. Instead of freaking out, think of them as a puzzle that you need to figure out. Eventually, if you play with the equations enough, you should be able to figure out the heat of reaction for just about any process.



### YOU'VE GOT PROBLEMS

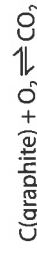
Problem 2: Find the heat of reaction for the following process:



Given the information:



$$\Delta H_{\text{rxn}} = -395.4 \text{ kJ}$$



$$\Delta H_{\text{rxn}} = -393.5 \text{ kJ}$$

The amount of energy required to raise the temperature of a substance by  $1^\circ\text{C}$  is called its heat capacity ( $C_p$ ). This is useful in calorimetry because if you know how much water is in the calorimeter and you know the heat capacity of water ( $4.184\text{ J/g}^\circ\text{C}$ ), you can calculate the amount of heat generated by the reaction in the bomb.

This equation is used to do this:

$$\Delta H = mC_p\Delta T$$

$\Delta H$  is the amount of energy transferred from the bomb to the water,  $m$  is the mass of water (in grams),  $C_p$  is the heat capacity of water ( $4.184\text{ J/g}^\circ\text{C}$ ), and  $\Delta T$  is the change in water temperature (in  $^\circ\text{C}$ ).

Let's see an example of a problem involving bomb calorimetry.

**Example:** I have set up a calorimetry experiment in which I will burn  $5.00\text{ g}$  of anthracene ( $\text{C}_{14}\text{H}_{10}$ ) in a bomb surrounded by  $2.00\text{ kJ}$  of water. If the temperature of the water rises by  $24.1^\circ\text{C}$ , what is the molar heat of combustion of anthracene?

**Solution:** The first step is to figure out how much energy this process released. Because you have  $2,000\text{ g}$  of water, its heat capacity is  $4.184\text{ J/g}^\circ\text{C}$ , and the temperature change is  $24.1^\circ\text{C}$ , you can use the previous equation to determine how much heat was transferred into the water:

$$\Delta H = mC_p\Delta T$$

$$\Delta H = (2,000\text{ g})(4.184\text{ J/g}^\circ\text{C})(24.1^\circ\text{C})$$

$$\Delta H = 202,000\text{ J}$$

But wait, there's more! You're trying to find the molar heat of combustion of anthracene, but you burned only  $5.00\text{ grams}$  of this substance. The molar mass of anthracene is  $178\text{ g/mol}$ , which means that you burned only  $0.0281\text{ mol}$  of it. To determine the molar heat of combustion, you need to divide the amount of energy in joules by the number of moles of anthracene to find the molar heat of combustion:

$$\frac{202,000\text{ J}}{0.0281\text{ mol}} = 7,190,000\text{ J/mol}$$

This is close to the actual value for the heat of combustion of anthracene,  $7,064\text{ kJ/mol}$ , probably due to some experimental error.

# Thermodynamics and Spontaneity

## Chapter 27

### In This Chapter

- Spontaneous processes
- Entropy
- Free energy

You might think that your understanding of enthalpy has made you into a superhero, able to leap tall reactions with a single bound. Well, I hate to break the news to you, but it just ain't so.

You see, there's more to thermodynamics than simple heats of reaction. As you learn in this chapter, heats of reaction play only one part in determining whether a reaction will occur spontaneously.

Read onward for more from the wonderful world of thermodynamics!

### Spontaneous Processes

Here's a pop quiz for you: Which of these processes might occur spontaneously?

- An apple falls upward, attaching itself to the branch of a tree.
- Water trickles down the side of a mountain after a rainstorm.
- Politicians speak honestly and forthrightly about important issues, making principled stands rather than just lying to make themselves look good.

If you guessed that only the second process occurs spontaneously, you already understand the idea of spontaneity. In the world of chemistry, just as in the previous examples, spontaneous processes are those that take place without outside intervention.

spontaneously flows into the second flask, leaving the system more random than before the valve was opened. The driving force for this process is entropy.

The behavior of entropy is spelled out by the *second law of thermodynamics*, which states that spontaneous processes are always accompanied by an increase in randomness (entropy) in the universe.



### DEFINITION

**The second law of thermodynamics** states that the entropy of the universe is always positive for spontaneous processes.

In math terms (because we all love math!), this is shown as the following for spontaneous processes:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Note that this equation doesn't say that the randomness of a system has to increase—just that the randomness of the *universe* has to increase.



### BAD REACTIONS

If you plug a vacuum cleaner into a wall and pick up huge quantities of dirt from the floor, your house is made less random. Though this appears to decrease the randomness of the universe, keep in mind that the processes used to generate the electricity that runs your vacuum cleaner caused a huge increase in the entropy of the universe! No process that increases the order in a system can take place unless it is caused by another process that creates an even larger disorder elsewhere in the universe.

It probably isn't a surprise to find that the entropy of a solid is less than that of a liquid, or that the entropy of a liquid is much less than that of a gas. After all, the molecules in a solid are locked tightly in place, the molecules in a liquid are close to each other but can move freely, and the molecules in a gas are flying all over the place and interact very little with one another. As a result, processes that create liquids from solids or gases from liquids are accompanied by an increase in entropy. The following puts this in mathematical terms:

$$\Delta S_{\text{solid}} < \Delta S_{\text{liquid}} \ll \Delta S_{\text{gas}}$$

**THE MOLE SAYS**

Recall that the little ° above the  $\Delta S$  term in the example reflects the fact that the reaction is taking place under standard conditions of 1 atm pressure, 298 K, and 1 M concentration for solutions, and that all solids and liquids are in their pure forms.

**Solution:** To solve this problem, you need to subtract the entropies of the reactants from the entropies of the products.

Reactants:

$$\Delta S^\circ \text{ for 2 mol C} = 2 \text{ mol} \times 5.7 \text{ J/mol K} = 11.4 \text{ J/K}$$

$$\Delta S^\circ \text{ for 3 mol H}_2 = 3 \text{ mol} \times 130.6 \text{ J/mol K} = 391.8 \text{ J/K}$$

$$\text{Total: } 403.2 \text{ J/K}$$

Products:

$$\Delta S^\circ \text{ for 1 mol C}_2\text{H}_6 = 1 \text{ mol} \times 229.5 \text{ J/mol K} = 229 \text{ J/K}$$

$$\Delta S^\circ_{\text{rxn}} = \Delta S^\circ_{\text{f}}(\text{products}) - \Delta S^\circ_{\text{f}}(\text{reactants})$$

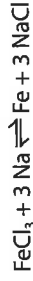
$$= 229.5 \text{ J/K} - 403.2 \text{ J/K}$$

$$= -173 \text{ J/K}$$

The result shows that the entropy change for this process is negative, which isn't surprising, considering that the reactants contain 3 mol of gas and the products consist of only 1 mol of gas. Because there are fewer moles of gas in the products than the reactants, you can expect the products to be more ordered than the reactants.

**YOU'VE GOT PROBLEMS**

Problem 1: Determine  $\Delta S^\circ_{\text{rxn}}$  for the following reaction:



The following information is given:

$$\Delta S^\circ(\text{FeCl}_3) = 142.3 \text{ J/mol K}$$

$$\Delta S^\circ(\text{Na}) = 51.3 \text{ J/mol K}$$

$$\Delta S^\circ(\text{Fe}) = 27.2 \text{ J/mol K}$$

$$\Delta S^\circ(\text{NaCl}) = 72.3 \text{ J/mol K}$$

## Calculating Changes in $\Delta G^\circ$

Just like entropy and enthalpy, you can find the free energy change for a reaction by subtracting the free energies of formation of the reactants from those of the products:

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f(\text{products}) - \Delta G^\circ_f(\text{reactants})$$

**Example:** Calculate  $\Delta G_{\text{rxn}}$  for the process:



Given that:

$$\Delta G^\circ_f(\text{CH}_4) = -50.8 \text{ kJ/mol}$$

$$\Delta G^\circ_f(\text{O}_2) = 0 \text{ kJ/mol}$$

$$\Delta G^\circ_f(\text{CO}_2) = -394.4 \text{ kJ/mol}$$

$$\Delta G^\circ_f(\text{H}_2\text{O}) = -228.6 \text{ kJ/mol}$$



### THE MOLE SAYS

Just as with enthalpy, the free energy of formation of a pure element is defined as zero.

**Solution:** To solve this problem, you need to subtract the free energies of the reactants from those of the products:

Reactants:

$$\Delta G^\circ_f \text{ for 1 mol CH}_4 = 1 \text{ mol} \times -50.8 \text{ kJ/mol} = -50.8 \text{ kJ}$$

$$\Delta G^\circ_f \text{ for 2 mol O}_2 = 2 \text{ mol} \times 0 \text{ kJ/mol} = 0 \text{ kJ}$$

$$\text{Total: } -50.8 \text{ kJ}$$

Products:

$$\Delta G^\circ_f \text{ for 1 mol CO}_2 = 1 \text{ mol} \times -394.4 \text{ kJ/mol} = -394.4 \text{ kJ}$$

$$\Delta G^\circ_f \text{ for 2 mol H}_2\text{O} = 2 \text{ mol} \times -228.6 \text{ kJ/mol} = -457.2 \text{ kJ}$$

$$\text{Total} = -851.6 \text{ kJ}$$

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f(\text{products}) - \Delta G^\circ_f(\text{reactants})$$

$$\Delta G^\circ_{\text{rxn}} = -851.6 \text{ kJ} - (-50.8 \text{ kJ})$$

$$\Delta G^\circ_{\text{rxn}} = -800.8 \text{ kJ}$$

This indicates that the combustion of methane is a spontaneous process.

Quantitatively, you can find the change in free energy for the process if you have  $\Delta H$ ,  $\Delta S$ , and the temperature using the equation  $\Delta G = \Delta H - T\Delta S$ .

**Example:** Find the change in free energy for the following reaction at 773 K, given the following information:

$$\Delta H^\circ_{\text{rxn}} = -483.6 \text{ kJ}$$

$$\Delta S^\circ_{\text{rxn}} = -88.8 \text{ J/K}$$

**Solution:** Before you can solve this problem, you need to convert  $\Delta S^\circ_{\text{rxn}}$  into units of kJ/K so that the units of both entropy and enthalpy are in kJ. To do this, you divide  $\Delta S^\circ_{\text{rxn}}$  by 1,000 and find that  $\Delta S^\circ_{\text{rxn}}$  is  $-0.0888 \text{ kJ/K}$ .

Placing the values for entropy, enthalpy, and temperature into the equation for free energy, you find the following:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -483.6 \text{ kJ} - (773 \text{ K} \times -0.0888 \text{ kJ/K})$$

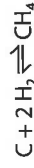
$$\Delta G = -483.6 \text{ kJ} + 68.6 \text{ kJ}$$

$$\Delta G = -415.0 \text{ kJ}$$



#### YOU'VE GOT PROBLEMS

Problem 2: Determine the free energy change for the following reaction at 500. K:



The following information is given:  $\Delta H^\circ_{\text{rxn}} = -74.8 \text{ kJ/mol}$ ;  $\Delta S^\circ_{\text{rxn}} = -80.6 \text{ J/K}$ .

## Free Energy and Pressure

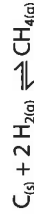
When calculating the standard free energy of a reaction, recall that the little  $^\circ$  over the  $\Delta G$  stands for the fact that the reaction takes place under standard conditions. For gases, “standard” conditions refers to a pressure of 1 atm. However, what happens when the pressures of gaseous reactants aren’t 1 atm?

I’m glad you asked! Though I won’t do the derivation, the free energy for a reaction when the pressures of gaseous reactants aren’t 1 atm is calculated using the following equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

**YOU'VE GOT PROBLEMS**

Problem 3: Determine the free energy change for the following reaction at 25°C:



When the partial pressure of hydrogen is 1.500 atm and the partial pressure of methane is 2.000 atm, the answer is  $\Delta G^\circ_{\text{rxn}} = -50.8 \text{ kJ/mol}$ .

## Relating Free Energy to the Equilibrium Constant

By looking at the magnitude of  $\Delta G^\circ$  for a process, you can get a pretty good feel for what the equilibrium constant,  $K$ , is for the reaction:

- When  $\Delta G^\circ = 0$ , the reaction is at equilibrium. At equilibrium the equilibrium constant  $K$  is equal to 1. As a result, when  $\Delta G^\circ = 0$ ,  $K = 1$ .
- When  $\Delta G^\circ$  is negative, the reaction is proceeding spontaneously. When a reaction proceeds spontaneously in the forward direction, the equilibrium constant for the process is greater than 1. As a result, when  $\Delta G^\circ < 0$ ,  $K > 1$ .
- When  $\Delta G^\circ$  is positive, the reaction doesn't proceed spontaneously in the forward direction, but it does spontaneously move backward from products to reactants. When a reaction goes backward, the equilibrium constant  $K$  is less than 1. As a result, when  $\Delta G^\circ > 0$ ,  $K < 1$ .

## The Least You Need to Know

- Spontaneous processes occur without any outside addition of energy.
- Increases in entropy (randomness) are a driving force for spontaneous processes.
- The free energy of a process is the final word on whether it can be spontaneous, and takes into account entropy, enthalpy, and temperature.
- Thermodynamics tells you whether a reaction will happen, while kinetics tells you how fast it will happen.
- The free energy and equilibrium constant of a given process are closely related.

# Solutions to “You’ve Got Problems”

## Appendix

# A

### Chapter 1

1. a) This is equal to  $7.5 \times 10^{-8}$  m, or  $75 \times 10^{-9}$  m, both of which are equal to 75 nm.  
b) This is equal to  $2.5 \times 10^7$  g, or  $25 \times 10^6$  g, or 2.5 Mg.
2. a) 45  $\mu\text{m}$  is equal to  $4.5 \times 10^{-5}$  m.  
b) 355 km is equal to  $355 \times 1,000$  m, or 355,000 m.

3. To solve, set up the following equation:

$$(160 \text{ pounds}) \left( \frac{1 \text{ kg}}{2.21 \text{ pounds}} \right) = 72 \text{ kg}$$

4. To solve this problem, set up your equation like this:

$$(555 \text{ ft}) \left( \frac{0.3048 \text{ m}}{1 \text{ ft}} \right) = 169 \text{ m}$$

5. To solve this problem, set up the equation:

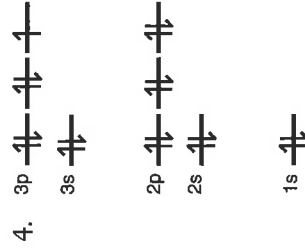
$$(25 \text{ miles}) \left( \frac{1.6 \text{ km}}{1 \text{ mile}} \right) \left( \frac{1000 \text{ m}}{1 \text{ km}} \right) = 4.0 \times 10^4 \text{ m}$$

6. This problem is solved by setting up the equation:

$$(340 \text{ cm}) \left( \frac{0.01 \text{ m}}{1 \text{ cm}} \right) \left( \frac{1 \mu\text{m}}{10^{-6} \text{ m}} \right) = 3.4 \times 10^6 \mu\text{m}$$

7. Any piece of equipment that’s not calibrated correctly may be precise but not accurate. Imagine that there’s a giant cockroach standing on the bottom of your bathroom scale. If you weigh yourself over and over again, you may get the same mass—however, this mass will always differ by the weight of the giant cockroach.

8. 6.24 mL



## Chapter 4

- Heterogeneous mixture
  - Homogeneous mixture
  - Heterogeneous mixture
  - Homogeneous mixture
- Keeping in mind the trend for electronegativity (it increases as you move left to right across a period and decreases as you move down a group), the trend, from lowest to highest, is  $Rb < Sn < P < O < F$ . Because the trend for atomic radius is to decrease across a period and increase across a group, you'd expect exactly the opposite trend:  $F < O < P < Sn < Rb$ .

## Chapter 5

- +2 (Magnesium will lose two electrons, to gain the same electron configuration as neon.)
  - +3 (Aluminum will lose three electrons, to gain the same electron configuration as neon.)
  - 1 (Bromine will gain one electron so that it has the same electron configuration as krypton.)

2.  $\ddot{\text{O}} \cdot \quad \cdot \ddot{\text{C}} \cdot \longrightarrow \cdot \ddot{\text{O}} \text{::} \text{C} \text{::} \ddot{\text{O}} \cdot$   
 $\quad \quad \quad \cdot \ddot{\text{O}} \cdot$
3. a) Phosphorus trichloride  
 b) Carbon monoxide  
 c) Sulfur hexafluoride  
 d) Silicon dioxide  
 e) Dinitrogen trioxide  
 f) Sulfur
4. a) HBr  
 b)  $\text{OCl}_2$   
 c)  $\text{Cl}_4$   
 d)  $\text{P}_2\text{O}_5$   
 e)  $\text{F}_2$   
 f)  $\text{B}_2\text{F}_4$

## Chapter 7

1.  $\begin{array}{c} \ddot{\text{N}}-\text{H} \\ | \\ \text{H} \end{array}$
2. a)  $\cdot \ddot{\text{O}} \text{=Si=}\ddot{\text{O}} \cdot$   
 b)  $\text{O}^{-1} \quad \cdot \ddot{\text{O}}-\text{H}$   
 c)  $\text{:N}\equiv\text{N:}$

2. a) Dipole-dipole forces  
b) London dispersion forces  
c) Hydrogen bonds  
d) London dispersion forces  
e) Dipole-dipole forces
3. Rank these from weakest to strongest intermolecular force. In this case, it's  $\text{CF}_4$  (London dispersion forces), followed by  $\text{PF}_3$  (with its dipole-dipole forces), followed by the highest boiling point for  $\text{HF}$  (which has hydrogen bonding as its main intermolecular force).

## Chapter 11

1. a) Yes. Water is polar and  $\text{LiCl}$  is an ionic compound.  
b) Yes. Both are polar.  
c) No. Carbon tetrachloride is nonpolar and ammonia is polar.
2. Because the molar mass of acetic acid is  $60.06 \text{ g/mol}$ , you have  $(120 \text{ g})/(60.06 \text{ g/mol}) = 2.0 \text{ mol}$  of acetic acid. Because you have  $3.1 \text{ L}$  of solution, the molarity is equal to  $2.0 \text{ mol}/3.1 \text{ L} = 0.65 \text{ M}$ .
3.  $45.0 \text{ g}$  of  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  is equal to  $0.284 \text{ mol}$ . Because  $560 \text{ mL}$  of water is equal to  $0.56 \text{ kg}$  of water, the molality of this solution is  $0.284 \text{ mol}/0.56 \text{ kg} = 0.51 \text{ m}$ .

$$4. \chi_{\text{H}_2\text{O}} = \frac{15.0 \text{ moles } \text{H}_2\text{O}}{15.0 \text{ moles } \text{H}_2\text{O} + 4.5 \text{ moles isopropanol}} = 0.77$$

5. Given that you'll use the equation  $M_1V_1 = M_2V_2$ ,  $M_1 = 0.500 \text{ M}$ ,  $V_1$  is unknown,  $M_2$  is  $0.125 \text{ M}$ , and  $V_2$  is  $750 \text{ mL}$ . Inserting these values into the equation, you get:

$$(0.500 \text{ M})(V_1) = (0.125 \text{ M})(750 \text{ mL})$$

$$V_1 = 190 \text{ mL}$$

Or, in other words, you need  $190 \text{ mL}$  of  $0.500 \text{ M NaCl}$  to make the desired solution.

5.  $PV = nRT$

$$(1.0 \text{ atm})(1,100 \text{ L}) = n (0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(523 \text{ K})$$

$$\underline{n} = 26 \text{ mol}$$

6. a) To find the number of moles of each gas, use  $PV = nRT$ :

Moles of oxygen:

$$PV = nRT$$

$$(5.0 \text{ atm})(55 \text{ L}) = \underline{n} (0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(288 \text{ K})$$

$$\underline{n} = 12 \text{ mol O}_2$$

Moles of nitrogen:

$$PV = nRT$$

$$(8.0 \text{ atm})(55 \text{ L}) = \underline{n} (0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(288 \text{ K})$$

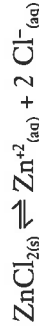
$$\underline{n} = 19 \text{ mol N}_2$$

b) The total pressure of gas in the container is simply the sum of the pressure of oxygen (5.0 atm) and the pressure of nitrogen (8.0 atm) given in the problem, for an answer of 13.0 atm.

## Chapter 14

1. Rubbing alcohol has a higher vapor pressure than iced tea.

2. When a solution is made by dissolving 2.5 mol of  $\text{ZnCl}_2$  in 2.0 kg of water, the molality of this solution is 2.5 mol/2.0 kg = 1.3 m. However,  $\text{ZnCl}_2$  dissociates into the  $\text{Zn}^{+2}$  and  $\text{Cl}^-$  ions using this equation:



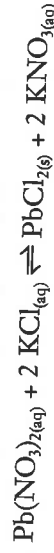
So the effective molality of the solution is three times as much as the previous calculation, or 3.9 m. Now, using the equation  $\Delta T_b = K_b m_{\text{solute}}$ , you find this:

$$\Delta T = (0.051^\circ \text{C/m})(3.9 \text{ m}) = 0.20^\circ \text{C}$$

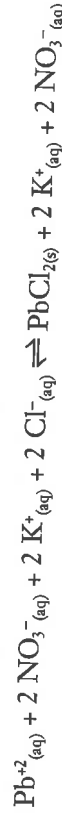
Thus, the final boiling point of the temperature has increased by  $0.20^\circ \text{C}$ , giving it a final boiling point of  $100.20^\circ \text{C}$ .

3. This is essentially the same type of problem as #2, except that 10.0 g of LiF have to be converted to moles (0.386 mol) and 850 mL of water have to be converted to kilograms (0.850 kg). This gives you a molality of 0.454 m.

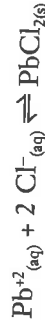
3. a) Double displacement reaction  
 b) Single displacement reaction  
 c) Acid-base reaction  
 d) Combustion reaction  
 e) Synthesis reaction
4. a)  $2 \text{NaOH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O}$   
 b)  $2 \text{NH}_3 + 3 \text{I}_2 \rightleftharpoons 2 \text{NI}_3 + 3 \text{H}_2$   
 c)  $2 \text{C}_3\text{H}_8\text{O} + 9 \text{O}_2 \rightleftharpoons 6 \text{CO}_2 + 8 \text{H}_2\text{O}$   
 d)  $2 \text{Na} + \text{FeSO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{Fe}$   
 e) No reaction will occur because both products are soluble in water.
5. Chemical equation:



Complete ionic equation:



Net ionic equation:



## Chapter 16

1.  $110.0 \text{ g NaCl} \times \left( \frac{1 \text{ mole NaCl}}{58.44 \text{ NaCl}} \right) \times \left( \frac{2 \text{ mole NaOH}}{2 \text{ mole NaCl}} \right) \times \left( \frac{40.00 \text{ g NaOH}}{1 \text{ mole NaOH}} \right) = 75.3 \text{ g NaOH}$
2. To solve this problem, you need to do two stoichiometry calculations. The first calculation will determine how much lead iodide can be formed from 115 g of lead nitrate. The second calculation will determine how much lead iodide can be formed from 265 g of potassium iodide. The smaller of these two numbers will be our answer. Let's get cracking:

3. Grinding coffee beans increases the surface area of the coffee that is in contact with the hot water, causing the coffee to brew more quickly.

## Chapter 18

1. From the data provided, you can see that the reaction rate is four times faster when the concentration of A is doubled ( $2.00 \times 10^{-5} / 5.00 \times 10^{-4} = 4$ ) and that the rate stays constant when the concentration of B is doubled. As a result, the reaction is second order in [A] and zeroth order in [B], resulting in the rate law:

$$\text{Rate} = k[A]^2$$

To find the rate constant, you can put the data from any of these experiments into the equation and solve for  $k$ . Let's use the data from experiment 1:

$$5.00 \times 10^{-6} \text{ M/s} = k (0.0100)^2$$

$$k = 5.00 \times 10^{-2} / \text{M}\cdot\text{s}$$

2. You can verify that this is a first-order reaction in [A] by graphing  $\ln[A]$  versus time. This graph produces a straight line:



The slope of this line is  $-k$ , or  $-(-0.0139/\text{M}\cdot\text{s})$  or  $0.0139/\text{M}\cdot\text{s}$ .

3. The equation that relates  $k$  to the half-life of a reaction is:

$$t_1 = \frac{0.693}{k}$$

Using the information in this problem, you find that:

$$65 \text{ sec} = \frac{0.693}{k}$$

$$k = 0.011 / \text{sec}$$

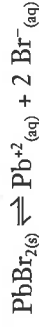
$$\begin{aligned} 4. \quad \ln \left( \frac{k_2}{k_1} \right) &= \left( \frac{E_a}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \left( \frac{12.2 \text{ L/mol}\cdot\text{s}}{2.50 \text{ L/mol}\cdot\text{s}} \right) &= \left( \frac{E_a}{8.31 \text{ J/K}\cdot\text{mol}} \right) \left( \frac{1}{1073 \text{ K}} - \frac{1}{1123 \text{ K}} \right) \\ 1.58 &= \left( \frac{E_a}{8.31 \text{ J/K}\cdot\text{mol}} \right) (4.149 \times 10^{-5}) \\ E_a &= 3.16 \times 10^5 \text{ J/mol} \end{aligned}$$

Taking the square root of both sides of this equation gives you:

$$2.24 = \frac{2x}{2.0 - x}$$

And solving for  $x$ , you get an answer of 1.06 M. Note that, in this example, you don't need to use the approximation that  $x$  is negligible when compared to 2 M when finding your answer.

2.  $\text{PbBr}_2$  dissociates according to the equation:



making your  $K_{sp}$  expression:

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^{-}]^2$$

When lead bromide dissociates, you find that the concentration of the bromide ion will be twice that of the lead ion because two bromide ions are created whenever  $\text{PbBr}_2$  breaks apart (as shown by the previous equation). As a result, you can say that the concentration of  $\text{Pb}^{2+}$  in a saturated solution is  $x$ , and the concentration of  $\text{Br}^{-}$  in the same solution is  $2x$ . Placing these values in your expression, you find:

$$K_{sp} = 2.1 \times 10^{-6} = [x][2x]^2$$

$$2.1 \times 10^{-6} = 4x^3$$

$$x = 8.1 \times 10^{-3} \text{ M}$$

As a result, the concentration of  $\text{Pb}^{2+}$  will be  $8.1 \times 10^{-3} \text{ M}$ , and the concentration of  $\text{Br}^{-}$  will be twice that, or  $1.6 \times 10^{-2} \text{ M}$ .

3. a) The reaction will shift toward products.
- b) The reaction will not shift at all.
- c) The reaction will shift toward products.
- d) The reaction will shift toward products.

## Chapter 20

1. a) Nitric acid
- b) Phosphoric acid
- c) Hydrophosphoric acid
- d) Hydrobromic acid

Because formic acid is a weak acid, you can make the assumption that  $x$  is a very small value compared to 0.750 M. This simplifies the expression such that:

$$1.77 \times 10^{-4} = \frac{[x][x]}{[0.750]}$$

which yields  $x = 0.115$  M.

To find the pH, place this value for  $[H^+]$  into the equation for pH:

$$\text{pH} = -\log[H^+]$$

$$\text{pH} = -\log[0.115 \text{ M}]$$

$$\text{pH} = 1.94$$

5. Because LiOH is a base, you need to use the equation  $K_w = [H^+][OH^-]$  to translate its concentration of  $OH^-$  to a concentration of  $H^+$  that fits into the equation  $\text{pH} = -\log[H^+]$ . When you do this, you find:

$$K_w = [H^+][OH^-]$$

$$1.00 \times 10^{-14} = [H^+][0.00340 \text{ M}]$$

$$[H^+] = 2.94 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[H^+]$$

$$\text{pH} = -\log[2.94 \times 10^{-12}]$$

$$\text{pH} = 11.5$$

6. To solve this problem, you must first find the concentration of  $OH^-$  ions using your knowledge of aqueous equilibria, then translate this concentration to a concentration of  $H^+$ , and finally use the equation for pH.

The equation for the dissociation of ammonium hydroxide is  $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ . Using the charts for finding equilibrium concentrations that you learned in Chapter 19, you find:

Species	Initial concentration (M)	Change (M)	Final concentration (M)
$NH_4OH$	0.00500	$-x$	$0.00500 - x$
$NH_4^+$	0	$+x$	$x$
$OH^-$	0	$+x$	$x$

## Chapter 21

1. a) Because bromine has a higher electronegativity than phosphorus, the oxidation state of bromine is the same as if it were an anion, or  $-1$  each. Because these three bromine atoms each have a  $-1$  oxidation state, the phosphorus atom has to have a  $+3$  oxidation state for the sum of the oxidation states to be zero.  
b)  $\text{NaOH}$  is an ionic compound. As a result,  $\text{Na}$  has a charge of  $+1$  and the sum of the charges on the hydroxide ion is  $-1$ . Given that hydrogen is bonded to a nonmetal, it must have a charge of  $+1$ . For the overall charge of the hydroxide ion to be  $-1$ , oxygen must have an oxidation state of  $-2$ .  
c) Each hydrogen has a  $+1$  oxidation state. Because oxygen is more electronegative than sulfur, each oxygen atom must have an oxidation state of  $-2$ . To make the sum of the oxidation states of all atoms in this molecule zero, sulfur must have an oxidation state of  $+6$  [ $+6 + (2)(+1) + (4)(-2)$ ] =  $0$ .  
d) Oxygen has a  $-2$  oxidation state as the more electronegative atom. For the molecule to be neutral, carbon must have a  $+2$  oxidation state.  
e) As the more electronegative atom, oxygen has a  $-2$  oxidation state. For the molecule to be neutral, carbon must have a  $+4$  oxidation state.
2. a) On the left side of the equation, carbon has a  $-4$  oxidation state, hydrogen has a  $+1$  oxidation state, and oxygen has an oxidation state of  $0$ . On the right side of the equation, carbon has a  $+4$  oxidation state, oxygen has a  $-2$  oxidation state (in both compounds), and hydrogen has a  $+1$  oxidation state. As a result, methane is the reducing agent (because carbon has been oxidized) and oxygen is the oxidizing agent (because oxygen was reduced).  
b) On the left side of the equation, copper has a  $0$  oxidation state, silver has a  $+1$  oxidation state, oxygen has a  $-2$  oxidation state, and nitrogen has a  $+5$  oxidation state. On the right side of the equation, silver has a  $0$  oxidation state, copper has a  $+1$  oxidation state, nitrogen has a  $+5$  oxidation state, and oxygen has a  $-2$  oxidation state. This means that, in this equation, copper is the reducing agent (copper was oxidized) and silver is the oxidizing agent (because silver was reduced).  
c) On the left side of this equation, sodium has a  $+1$  oxidation state, oxygen has a  $-2$  oxidation state (in both compounds), hydrogen has a  $+1$  oxidation state, and sulfur has a  $+6$  oxidation state. Looking at the right side of the equation, we find that none of these oxidation states has changed. This means that this reaction, while interesting, is not a redox reaction at all!

4. The oxidation reaction is  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ . Because the standard reduction potential for this process is  $-1.66\text{ V}$ , the half-cell potential for the oxidation is  $+1.66\text{ V}$ . For the reduction reaction  $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ , the standard reduction potential is  $-0.44\text{ V}$ . As a result, the standard cell potential for this voltaic cell is  $1.66\text{ V} - 0.44\text{ V} = 1.22\text{ V}$ .

5. The cell described by the equation  $\text{Cu}|\text{Cu}^+||\text{Co}^{3+}|\text{Co}^{+2}$  has the equation  $\text{Cu} + \text{Co}^{3+} \rightarrow \text{Cu}^+ + \text{Co}^{+2}$ . Setting up  $Q$  for this reaction and remembering that you ignore the concentration of  $\text{Cu}$  because it's a solid, you find:

$$Q = \frac{[\text{Cu}^+][\text{Co}^{+2}]}{[\text{Co}^{3+}][\text{Cu}]} = \frac{[1.50M][0.55M]}{[0.65M]} = 1.3$$

To solve this problem using the Nernst equation, we also need the standard cell potential for this process. The oxidation reaction is  $\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^-$ , which has a reduction potential of  $0.52\text{ V}$  and a half-cell potential of  $-0.52\text{ V}$ . The reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{+2}$  has a reduction potential of  $1.82\text{ V}$ . When you add  $-0.52\text{ V}$  to  $1.82\text{ V}$ , you find that the standard cell potential for this process is  $1.30\text{ V}$ .

Plugging these values into the Nernst equation, you find:

$$E = E^0 - \frac{0.0591}{n} \log Q$$

$$E = 1.30V - \frac{0.0591}{1} \log(1.3)$$

$$E = 1.30V - 0.0067V$$

$$E = 1.29V$$

## Chapter 22

1. a) Hexaaquanickel (II) chloride
- b) Potassium tetrachloronickelate (0)
- c) Lithium hexacyanoaluminate (III)

the carbon atoms are  $sp^3$  hybridized and want a bond angle of  $120^\circ$ . Because cyclopropene is farther from its desired bond angle than cyclopropane, it is a less stable molecule.

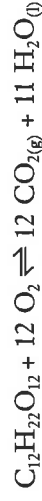
5. The carbon at the 3 position has a methyl group, an ethyl group, a hydrogen (which isn't shown), and that big ugly group on the left all stuck to it. Because four different things are stuck to this atom, this is a chiral molecule.

## Chapter 25

- ${}_{47}^{108}\text{Ag} \rightarrow {}_{-1}^0\text{e} + {}_{48}^{108}\text{Cd}$
  - ${}_{86}^{216}\text{Rn} \rightarrow {}_2^4\text{He} + {}_{84}^{212}\text{Po}$
- $t_{\frac{1}{2}} = \frac{0.693}{k}$   
 $k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{74.6 \text{ yrs}} = 0.00929 / \text{yr}$
  - $\ln[A_t] = -kt + \ln[A_o]$   
 $\ln[A_t] = -(0.00929)(675 \text{ yr}) + \ln(85.0 \text{ g})$   
 $\ln[A_t] = -6.27 + 4.44$   
 $\ln[A_t] = -1.83$   
 $[A_t] = 0.16 \text{ g}$

## Chapter 26

- The equation for this reaction is:



**Products:**

$$\Delta H_f^\circ \text{ for } 12 \text{ mol CO}_2 = 12 \text{ mol} \times -393.5 \text{ kJ/mol} = -4,722 \text{ kJ}$$

$$\Delta H_f^\circ \text{ for } 11 \text{ mol H}_2\text{O} = 11 \text{ mol} \times -285.8 \text{ kJ/mol} = -3,144 \text{ kJ}$$

$$\text{Total: } -7,866 \text{ kJ}$$

**Products:**

$$\Delta S^\circ \text{ of 1 mol Fe} = 1 \text{ mol} \times 27.2 \text{ J/mol K} = 27.2 \text{ J/K}$$

$$\Delta S^\circ \text{ of 3 mol NaCl} = 3 \text{ mol} \times 72.3 \text{ J/mol K} = 216.9 \text{ J/K}$$

$$\text{Total: } 244.1 \text{ J/K}$$

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \Delta S^\circ_{\text{products}} - \Delta S^\circ_{\text{reactants}} \\ &= 244.1 \text{ J/K} - 296.2 \text{ J/K} \\ &= -52.1 \text{ J/K}\end{aligned}$$

2. As in the example in the chapter, you need to convert the units of  $\Delta S^\circ_{\text{rxn}}$  to kJ/K so that the units of entropy and enthalpy are the same. Dividing by 1,000,  $\Delta S^\circ_{\text{rxn}} = -0.0806 \text{ kJ/K}$ .

Placing the values for entropy, enthalpy, and temperature into the equation for free energy:

$$\Delta G = \Delta H - T\Delta S$$

$$= -74.8 \text{ kJ} - (500 \text{ K} \times -0.0806 \text{ kJ/K})$$

$$= -74.8 \text{ kJ} + 40.3 \text{ kJ}$$

$$= -34.5 \text{ kJ}$$

3. Before you can determine the change in free energy, you need to figure out what the reaction quotient is. Using the definition of reaction quotient, you find:

$$Q = \frac{(P_{\text{CH}_4})}{(P_{\text{H}_2})^2} = \frac{(2.000 \text{ atm})}{(1.500 \text{ atm})^2} = 0.8889$$

*Note:* The "pressure" of carbon isn't included in the expression for reaction quotient because carbon is a solid.

Using the equation  $\Delta G = \Delta G^\circ - RT \ln Q$ , you get:

$$\begin{aligned}\Delta G &= -50.8 \text{ kJ/mol} - (8.314 \text{ J/K mol})(298 \text{ K}) \ln (0.8889) \\ &= -50.8 \text{ kJ/mol} - (-292 \text{ J/mol})\end{aligned}$$

Because  $-292 \text{ J/mol} = -0.292 \text{ kJ/mol}$ , you get:

$$\begin{aligned}\Delta G &= -50.8 \text{ kJ/mol} + 0.292 \text{ kJ/mol} \\ &= -50.5 \text{ kJ/mol}\end{aligned}$$

## Glossary

## B

**absorption** (1) In spectroscopy, condition in which light is used to push an electron from a ground state to an excited state. (2) Condition in which a chemical is soaked up by a material, similar to water being absorbed into paper towels.

**accuracy** A measured value being close to the actual value. Accurate measurements are also precise.

**acid** Any material that can accept a pair of electrons. In aqueous solutions, those with  $\text{pH} < 7.00$ .

**acid dissociation constant ( $K_a$ )** The constant that describes the equilibrium position for the dissolution of an acid in water.

**acid-base reaction** An electron pair is donated by a base to an acceptor acid. In an aqueous solution, the reaction of  $\text{H}^+$  and  $\text{OH}^-$  yields water.

**actinides** The 5f group of the periodic table, consisting of elements Ac through No.

**activation energy** The minimum amount of energy that's required for the reactants of a chemical reaction to form products.

**adsorption** Condition in which a chemical is stuck to the surface of a material.

**alkali metals** All elements in group 1 of the periodic table, except hydrogen. Alkali metals are the most reactive group of metals.

**alkaline earth metals** Reactive elements in group 2 of the periodic table.

**alkane** A hydrocarbon that contains only single carbon-carbon bonds. Also called a saturated hydrocarbon.

**alkene** A hydrocarbon that contains at least one double bond.

**alkyne** A hydrocarbon that contains at least one triple bond.

**alloy** A metal in which several elements are present.

- Avogadro's law** The molar volumes of all ideal gases are the same.
- Avogadro's number** The number of objects in a mole,  $6.02 \cdot 10^{23}$ .
- base** Any molecule that can donate a pair of electrons to form a bond. In aqueous solutions, those with  $\text{pH} > 7.00$ .
- beta decay** Condition in which an electron (called a "beta particle" in this context) is emitted during the radioactive decay of an atomic nucleus.
- bidentate ligands** Ligands that donate two electron pairs to a transition metal ion.
- binding energy** The energy due to the mass defect of an atom. It's responsible for holding the nucleus together.
- biochemistry** The study of chemistry as it occurs in living organisms.
- Bronsted-Lowry acid** A compound that gives  $\text{H}^+$  ions to other compounds.
- Bronsted-Lowry base** A compound that accepts  $\text{H}^+$  ions from other compounds.
- buffer** A solution consisting of a weak acid and its conjugate base that resists changes in pH when acid or base is added to it.
- buffering capacity** The quantity of acid or base that can be added to a buffered solution before the pH undergoes significant change.
- calorimetry** The process by which the energy change of a process is experimentally determined.
- catalyst** A material that increases the rate of a chemical reaction without being consumed.
- cathode** The electrode at which reduction occurs.
- cation** An atom or group of atoms with positive charge.
- cell potential** A measure of the electromotive force that drives electrons in a voltaic cell.
- chelate** A ligand that can donate more than one electron pair to a metal ion. The best known of the chelating agents is ethylenediamine, usually abbreviated as (en).
- chiral** A molecule with "handedness," in which atoms are arranged in similar fashion but can't be superimposed on top of one another.
- chromatography** A method of separating a mixture in which the components are passed through a third material. The affinity of each component of the mixture to stick to this third material determines how long it takes for it to travel through the material.

- cycloalkane** An alkane in which the carbon atoms are arranged in a ring.
- d-transition metals** The metallic elements in groups 3–12 of the periodic table.
- DNA** Deoxyribonucleic acid, the basic method of coding genetic information.
- decomposition reaction** Large molecules breaking apart to form smaller molecules.
- dehydration** The reversible removal of water molecules from hydrates to form anhydrides.
- denaturing** Extreme changes in pH or heat that cause enzymes to stop functioning.
- deposition** The process by which a gas becomes a solid without first becoming a liquid.
- determinate error** See systematic error.
- differential rate law** A rate law that explains the relationship between the concentration of the reactants and the reaction rate.
- diffusion** The rate at which a gas travels across a room.
- dilution** The process by which a solvent is added to a solution to make the solution less concentrated.
- dipole-dipole force** An attractive force caused when the partially negative side of one polar molecule interacts with the partially positive side of another.
- dissociation** Fancy word for “dissolving.”
- distillation** A process in which a mixture of materials is heated to separate them. One material vaporizes more quickly than the other, allowing them to be separated.
- doping** A method by which the conductivity of semiconductors is increased by adding a small amount of another element.
- double displacement reaction** A reaction that occurs when the cations of two ionic compounds switch places.
- effusion** The rate at which a gas escapes through a small hole in a container.
- electrode** The location of oxidation or reduction in a voltaic cell.
- electrolysis** The process by which a current is forced through a cell to make a non-spontaneous electrochemical change occur.
- electrolyte** A compound that, when dissolved, causes water to conduct electricity.
- electron** Negatively charged particles that are found in the orbitals outside the nucleus of an atom.

**exothermic** A reaction that releases heat.

**extraction** A process by which a mixture of materials is shaken with a solvent to separate them. The separation occurs because one material is more soluble in the new solvent than the other.

**f-transition metals** Another term for the lanthanides (elements 57–70) and actinides (elements 89–102).

**family** *See* group.

**ferromagnetic materials** Materials that can form permanent magnets.

**first law of thermodynamics** *See* law of conservation of energy.

**fission** An atomic nucleus breaking apart to make two smaller ones and a huge amount of energy.

**free energy (G)** Gibbs free energy, which is comprised of enthalpy (heat) and entropy (randomness). G is the fundamental measure that determines the position of equilibria and the rates of reactions. It is usually expressed in kJ/mol.

**free radical** An atom or group of atoms with an unpaired electron.

**fusion** A nuclear process in which small nuclei combine to make larger ones plus a huge quantity of energy.

**gamma ray** Very high energy electromagnetic radiation that's frequently given off when a nucleus undergoes radioactive decay.

**gas** The phase of matter in which particles are usually very far apart from one another, move very quickly, and aren't particularly attracted to one another.

**geometric isomers** Two or more structures that have the same formula and bond types (single, double, and so on) but differ in geometry (groups bonded to opposite sides of cyclic structures or double bonds). Geometric isomers are sometimes included in the generic term *stereoisomers*.

**ground state** The orbital in which an electron is found if energy is not added to the atom.

**group** A column in the periodic table. Elements in the same group have similar chemical and physical properties.

**half-cell** The chemical process that takes place at one of the electrodes in a voltaic cell.

**half-life ( $t_{1/2}$ )** The amount of time it takes for half of the reactant to be converted to product in a first-order chemical or nuclear process.

**integrated rate law** A rate law that describes how the concentrations of the reactants in a chemical reaction vary over time.

**intermediate** A chemical that was formed by one step in a reaction mechanism that will be consumed in another.

**intermolecular force** A force that holds covalent molecules to one another.

**ion** A particle with either positive or negative charge.

**ion product constant ( $K_w$ )** Equal to  $10^{-14}$ , it's the product of the  $H^+$  and  $OH^-$  concentrations in an aqueous solution.

**ionic compound** A compound formed when a cation and anion combine with one another.

**ionization energy** The amount of energy required to pull one electron off an atom.

**isomers** Different molecules with the same formulas.

**isotopes** Atoms of the same element that have different masses. These different masses are due to differing numbers of neutrons in the nucleus.

**$K_a$**  The acid dissociation constant, which describes the position of the equilibrium  $HA \rightleftharpoons H^+ + A^-$ .

**kinetic energy** Energy caused by the motion of an object.

**kinetics** The study of reaction rates.

**lanthanides** The 4f section of the periodic table, consisting of the elements La through Yb.

**law of conservation of energy** Energy can neither be created nor destroyed in any process.

**law of conservation of mass** The weights of reactants in a chemical reaction are the same as the weights of the products. No matter what chemical changes may occur, matter is neither created nor destroyed.

**law of definite composition** A chemical compound contains the same elements in the same proportions by mass, regardless of how it was made.

**law of multiple proportions** When two elements form more than one chemical compound, the ratios of the mass of one element that combines with a fixed mass of the other element can be expressed as a ratio of small, whole numbers.

**Le Châtelier's principle** If you change the conditions of an equilibrium, the equilibrium will shift in a way that minimizes the effects of whatever you did.

- molar volume** The volume of 1 mol of any gas at standard temperature and pressure.
- molarity (M)** Moles of solute per liters of solution.
- mole**  $6.02 \times 10^{23}$  things.
- mole fraction ( $\chi$ )** The number of moles of one component in a solution divided by the total number of moles of all components in the mixture.
- mole ratio** The ratio of moles of product to the ratio of moles of reactant of a chemical reaction.
- molecular solid** A material consisting of many covalent molecules held together by intermolecular forces.
- molecular weight** See molar mass.
- molecularity** The number of reactant molecules that combine in a chemical process.
- molecule** A group of atoms held together with covalent bonds.
- monodentate ligand** A ligand that donates one electron pair to a transition metal ion.
- monosaccharide** A simple sugar, such as glucose or fructose.
- network atomic solid** A material in which many atoms are bonded together covalently to form one gigantic molecule.
- neutrons** Neutral particles with a mass of about 1 amu that are found in the nucleus of an atom.
- noble gases** Group 18 on the periodic table, noted for unreactivity.
- normal boiling point** The temperature at which a liquid boils at a pressure of 1.00 atm.
- normality (N)** The number of moles of a reactive species per liter of solution.
- nucleon** The particles in the nucleus of an atom, namely protons and neutrons.
- nucleus** The center of an atom, where the protons and neutrons are found.
- nuclide** Term that describes a particular isotope of an element.
- octet rule** Elements tend to want to gain or lose electrons to attain the same electron configurations as the nearest noble gas.
- orbital** Regions of space outside the nucleus of an atom in which electrons can be found.
- order** An exponential term in a rate law that describes how the overall rate of the reaction depends on the concentration of each reactant.

**polysaccharide** A sugar that consists of long chains of simple sugars. Examples of polysaccharides include carbohydrates such as starch, glycogen, and cellulose.

**positron** The antimatter equivalent of an electron. It has a positive charge and is created during positron decay.

**potential energy** Stored energy. In chemical processes, it's frequently stored in chemical bonds.

**precision** When a value can be measured repeatedly. High precision in a measurement usually (but not always) indicates high accuracy.

**pressure** The amount of force exerted by the particles in a gas as they hit the sides of a container.

**primary structure** For proteins, this is a list of the amino acids that went into making the protein.

**principal quantum number** Denoted by  $n$ , it describes the energy level of an electron. Possible values are 1, 2, 3 ...  $n$ .

**probability distribution** A graph that shows how the electron density of an orbital is related to the distance from the nucleus.

**product** The final result of a chemical reaction.

**protein** A large molecule formed by the combination of amino acids.

**protons** Positively charged particles with a mass of about 1 amu that are found in the nucleus of an atom.

**qualitative data** Observations that can't be expressed as numbers ("My cat is ugly").

**quantitative data** Any measurements that involve numbers, such as weights, lengths, times, or temperatures.

**quaternary structure** The structure in which proteins wind themselves around other proteins, as in hemoglobin.

**RNA** Ribonucleic acid, which has a wide variety of functions in cells. RNA differs structurally from DNA, in that the main sugar is ribose and not deoxyribose, and it is a single chain rather than a double helix.

**radiation** The small particles emitted during the radioactive decay of an atomic nucleus.

**radioactive decay** When a nucleus spontaneously breaks apart to form smaller particles.

**secondary structure** In proteins, the larger arrangement into which the protein chain winds itself.

**semiconductor** A material through which electricity flows well only at high temperatures or voltages.

**SI units** The standard metric system of units.

**significant figures** The number of digits in a measured or calculated value that gives meaningful information about what's being measured or calculated.

**single displacement reaction** A pure element switches places with one of the elements in a chemical compound.

**solid** The state of matter in which the atoms or molecules are locked into place by either chemical bonds or intermolecular forces.

**solubility product constant ( $K_{sp}$ )** The equilibrium constant for the dissociation of a solute into a solvent.

**solute** What gets dissolved in a solution.

**solution** See homogeneous mixture.

**solvent** The major component that dissolves a solute. Solvents are usually liquids but can also be solids.

**specific heat ( $C_p$ )** The amount of energy required to heat 1 g of a substance by 1 K at constant pressure.

**spectroscopy** A method of identifying unknown substances from their spectra.

**spectrum** A pattern of light that corresponds to the movement of electrons between the ground and excited states. The plural of spectrum is *spectra*.

**spin quantum number** Denoted by  $m_s$ , it distinguishes between the two electrons in an orbital. Possible values are  $+\frac{1}{2}$  and  $-\frac{1}{2}$ .

**spontaneous** A process that takes place without outside intervention.

**standard conditions** For gases, 1 atm and 273 K; for liquids, 1 M and 273 K.

**standard temperature and pressure (STP)** 0° C (273 K) and 1 atm.

**stereoisomers** Isomers that differ in three-dimensional structure from one another.

**stoichiometry** The method used to relate the masses or volumes of the reactants and products of a chemical reaction to each other.

**unsaturated solution** A solution that hasn't yet dissolved the maximum possible quantity of solute.

**unshared electron pair** See lone pair.

**valence electrons** The number of s- and p- electrons beyond the most recent noble gas.

**valence shell electron pair repulsion (VSEPR) theory** The shapes of covalent molecules depend on the fact that pairs of valence electrons tend to repel each other.

**vapor pressure** The vapor pressure of a liquid is the gas pressure in a closed container due to the molecules that have evaporated from the liquid.

**voltaic cell** Fancy word for "battery."

**volume** A measure of how much space an object occupies. In chemistry, it's usually measured in milliliters or liters.

**weak** Used to describe acids, bases, and electrolytes, it indicates that the compound in question only partially dissociates in water.

**zwitterion** A compound that can have a positive charge on one atom and a negative charge on another.

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