CHE 104: PRINCIPLES OF CHEMISTRY II



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This text was compiled on 03/11/2026

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Licensing

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1.1: Redox Reactions and Oxidation Numbers

Redox reactions are a type of chemical reactions in which there is a change of oxidation numbers between reactants and products. The **oxidation number** (O.N.) of an element represents the total number of electrons which have been *removed* (a positive oxidation state) or *added* (a negative oxidation state) to get the element into its present state. The term **oxidation** describes the *loss* of electrons by an element and an *increase* in oxidation state; the term **reduction** describes the *gain* of electrons and a *decrease* in oxidation state. Oxidation numbers for elements in compounds can be calculated using a simple set of rules, which are reproduced below in Table 5.3.

Table 5.3 Rules for Assigning Oxidation Numbers
1. The oxidation number of an element in the free state is **zero**.
2. A monoatomic ion will have an oxidation number that is equal to its charge.
3. In most compounds, the oxidation number of hydrogen is **+1** (exception: when hydrogen is bonded to a metal, the oxidation number **-1**.)
4. Oxygen, within a compound, will generally have an oxidation number of **–2** (exception: in peroxides, the oxidation number of oxygen is -1)
5. The oxidation numbers of combined elements from groups I and II are +1 and +2, respectively.
6. The algebraic sum of oxidation numbers of all elements in a neutral compound formula equals zero.
7. The algebraic sum of the oxidation numbers of all elements in a polyatomic ion is equal to the charge of the ion

In many chemical reactions, the oxidation number of elements change. Consider the synthesis reaction shown below. In the reactants, carbon and oxygen are both elements and their oxidation numbers are zero (Rule 1). In the product, oxygen will have an oxidation number of –2 (Rule 4), therefore, carbon in CO_2 must have an oxidation number of +4 in order to balance the four negative charges on the oxygens. During this reaction, the oxidation number of carbon has changed from zero in the reactants to +4 in the products and the oxidation number of oxygen has changed from zero to –2. This is an example of a **redox reaction**; **a chemical reaction in which the oxidation numbers of elements change on going from reactants to products.**

$$\mathbf{C}\ \textit{(s)} + \mathbf{O_2}\ \textit{(g)} \rightarrow \mathbf{CO_2}\ \textit{(g)}$$

In a redox reaction, the element that "**loses electrons**" is said to be **oxidized** and will have *an increase in its oxidation number*. In the example above, the oxidation number of carbon *increases* from zero to +4; it has "lost electrons" and has been **oxidized**. The element that "**gains electrons**" in a redox reaction is said to be **reduced** and will have a *decrease in its oxidation number*. In the reaction above, the oxidation number of oxygen has *decreased* from zero to –2; it has "gained electrons" and has been **reduced**.

An examination of the rules for assigning oxidation numbers reveals that there are many elements for which there are no specific rules, such as nitrogen, sulfur, and chlorine. These elements, as well as some others, can have variable oxidation numbers depending on the other atoms to which they are covalently bonded in a molecular compound. It is useful to analyze a few molecules in order to see the strategy to follow in assigning oxidation numbers to other atoms.

Oxidation numbers for the atoms in a binary ionic compound are easy to assign because they are equal to the charge of the ion (rule 2). In $CuCl_2$, the oxidation number of copper is +2, while the oxidation number of chlorine is −1. This is because $CuCl_{2\ is}$ an ionic compound that is actually composed of these ions.

Assigning oxidation numbers for molecular compounds is trickier. The key is to remember rule 6: that the sum of all the oxidation numbers for any neutral species must be zero. Make sure to account for any subscripts which appear in the formula. As an example, consider the compound nitric acid, HNO_3. According to rule 3, the oxidation number of hydrogen is +1. According to rule 4, the oxidation number of oxygen is −2. There is no rule regarding nitrogen, but its oxidation number can be calculated as follows.

$1(+1)+x+3(-2)=0$, where x is the oxidation number of nitrogen.

Solving for x, we obtain $x=+5$

The oxidation number of the nitrogen atom in HNO_3 is +5

Examples 1.1.1

For each of the reactions given below, calculate the oxidation number of each of the elements in the reactants and the products and determine if the reaction involves oxidation-reduction. If it is a redox reaction, identify the elements that have been oxidized and reduced.

a. $Cu_2S \rightarrow 2\ Cu + S$
Reactants: Cu O.N.= +1 S O.N. = -2
Products: Cu O.N.= 0 S O.N.= 0
Element oxidized: sulfur Element Reduced: copper. This is a redox reaction.

b. $CaCO_3 \rightarrow CaO + CO_2$
Reactants: Ca O.N.= +2 C O.N.= +4 O O.N.= -2
Products: Ca O.N.= +2 C O.N.= +4 O O.N.= -2
Element oxidized: none. Element Reduced: none. This is non-redox reaction.

c. $Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O$
Reactants: Fe O.N.=+3 O O.N.=-2 H O.N.=0
Products: Fe O.N.=0 O O.N.=-2 H O.N.=+1
Element oxidized: hydrogen. Element Reduced: iron. This is a redox reaction

d. $AgNO_3 + NaCl \rightarrow AgCl\ (s) + NaNO_3$
Reactants: Ag O.N.=+1 (cation) N O.N.=+5 (rule 6) O O.N.=-2 Na O.N.=+1 Cl O.N.=-1
Ag O.N.=+1 (cation) N O.N.=+5 (rule 6) O O.N.=-2 Na O.N.=+1 Cl O.N.=-1
Element oxidized: none. Element Reduced: none. This is a non-redox reaction

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1.2: Oxidation-Reduction Half-Reactions

Learning Objectives

- To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous $\mathbf{HCl}$, the following reaction occurs (Figure 1.2.1):

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq)} \tag{1.2.1}$$

This is one example of what is sometimes called a *single replacement reaction* because $\mathbf{Zn}$ replaces $\mathbf{H}$ in combination with $\mathbf{Cl}$.



Figure 1.2.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 1.2.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

zinc atoms are oxidized to Zn^{2+}. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance:

the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced **reduction half reaction** is as follows:

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{array}{r} Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ \underline{2H^+ + \cancel{2e^-} \rightarrow H_2} \\ Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{array}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel**. The following example demonstrates this process.

Example 1.2.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^+ + Al \longrightarrow Ag + Al^{3+}$$

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

Reduction half-reaction:

$$Ag^+ + e^- \longrightarrow Ag$$

Aluminum is oxidized, losing three electrons to change from Al to Al^{3+}:

Oxidation half-reaction:

$$Al \longrightarrow Al^{3+} + 3\,e^-$$

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$\begin{array}{r} 3\left(Ag^+ + e^- \rightarrow Ag\right) \\ \underline{Al \rightarrow Al^{3+} + 3e^-} \\ 3Ag^+ + Al \rightarrow 3Ag + Al^{3+} \end{array}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+
- The **reducing agent** is the same as the substance oxidized: Al

- The **oxidizing agent** is the same as the substance reduced: $\mathbf{Ag^+}$

Exercise 1.2.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: $\mathbf{Ca^{2+} + 2\,e^- \longrightarrow Ca}$

Oxidation: \(2 \times (\ce{K -> K^{+} + e^{-}})\)

Combined: $\mathbf{Ca^{2+} + 2\,K \longrightarrow Ca + 2\,K^+}$

- The **substance oxidized** is the reactant that had undergone oxidation: $\mathbf{K}$
- The **substance reduced** is the reactant that had undergone reduction: $\mathbf{Ca^{2+}}$
- The **reducing agent** is the same as the substance oxidized: $\mathbf{K}$
- The **oxidizing agent** is the same as the substance reduced: $\mathbf{Ca^{2+}}$

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathbf{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)_2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in $\mathbf{NiOOH}$ are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathbf{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure **1.2.1**: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule

loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

Example 1.2.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \longrightarrow NH_3$
b. $CH_3CH_2OHCH_3 \longrightarrow CH_3COCH_3$
c. $HCHO \longrightarrow HCOOH$

Solution

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 1.2.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \longrightarrow CO_2 + H_2O$
b. $NO_2 \longrightarrow N_2$
c. $CH_2{=}CH_2 \longrightarrow CH_3CH_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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1.3: Balancing Redox Equations

Balancing Redox Equations using Half-reactions

Another way to balance redox reactions is by the half-reaction method. This technique involves breaking an equation into its two separate components - the oxidation reaction and the reduction reaction. Since neither oxidation nor reduction can actually occur without the other, we refer to the separate equations as **half-reactions**.

The general technique involves the following:

- The overall equation is broken down into **two** half-reactions. If there are any spectator ions, they are removed from the equations.
- Each half-reaction is balanced separately - first for atoms and then for charge. Electrons are added to one side of the equation or the other in order to balance charge. For example, if the reactant side of the equation has a total charge of +3, the product side must also equal +3.
- Next the two equations are compared to make sure electrons lost equal electrons gained. One of the half reactions will be an oxidation reaction, the other will be a reduction reaction.
- Finally the two half-reactions are added together, and any spectator ions that were removed are placed back into the equation

Consider the following reaction:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \tag{1.3.1}$$

In this reaction, Mg is oxidized and Cl is reduced. You may find it useful to use oxidation numbers to help you determine this. Mg changes from 0 to +2; Cl changes from 0 to -1.

When we write the half-reactions,we break apart compounds that contain either of the key elements (elements undergoing oxidation or reduction). Oxidation numbers are written as if they were ion charges. Notice that the chlorine from $MgCl_2$ is written as two separate ions, not combined as is Cl_2. Balance the two reactions for atoms.

$Mg \rightarrow Mg^{+2}$	$Cl_2 \rightarrow 2\ Cl^-$

Next balance the equations for charge by adding electrons. Remember - one half-reaction will be an oxidation reaction (electrons on the product side) and the other will be reduction (electrons will be on the reactant side)

$Mg \rightarrow Mg^{+2} + 2\ e^-$	$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$
oxidation	**reduction**

In this example, balancing for charge results in both sides, of both equations, having net charges of 0. That won't always be the case. Be sure you see in this example how charges are balanced.

We then compare the two equations for numbers of electrons. We see that both equations have 2 electrons so we do not need to make any adjustments for that. Finally, add the two equations together:

$$Mg + Cl_2 \rightarrow Mg^{+2} + 2Cl^- \tag{1.3.2}$$

and reform any compounds broken apart in the earlier steps:

$$Mg + Cl_2 \rightarrow MgCl_2 \tag{1.3.3}$$

We see that the original equation was already balanced, not just for atoms but for electrons as well.

Example 2

$$Cu_{(s)} + AgNO_{3(aq)} \rightarrow Cu(NO_3)2(aq) + Ag_{(s)} \tag{1.3.4}$$

Solution

Identify the elements undergoing oxidation (Cu) and reduction (Ag). The nitrate group (NO_3) is a spectator ion which we will not include in our half-reactions.

$Cu \rightarrow Cu^{+2} + 2\ e^-$	$Ag^+ + 1\ e^- \rightarrow Ag$
oxidation	**reduction**

After balancing for atoms and for charge, we see that the two equations do not have the same number of electrons - there are 2 in the copper reaction but only one in the silver reaction. Multiply everything in the silver reaction by 2, then we will add the equations together:

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions	**Balance electrons**	**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2\ e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2\ e^-}$
$Ag + 1\ e^- \rightarrow Ag^-$	$\times 2$	$2\ Ag^+ + \cancel{2e^-} \rightarrow 2\ Ag$
Add equations together		$Cu + 2\ Ag^+ \rightarrow Cu^{+2} + 2\ Ag$
Reform compound/return spectator ions		**$Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag$**

Here is a reaction occurring in an acid solution, which accounts for the presence of the H^+ions. This example adds a little more complexity to our problem.

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

In this example, spectator ions have already been removed. Even though hydrogen and oxygen do not undergo changes in oxidation number they are not spectators and we need to work with them in our half-reactions.

We determine that Mn undergoes reduction (+7 to +2) while Fe undergoes oxidation (+2 to +3). The iron half-reaction is straight forward, but the manganese reaction is more complex - we must include hydrogen and oxygen in its half-reaction:

$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$
oxidation	**reduction**

To balance the manganese half-reaction - first balance for Mn and O atoms. Next balance the H atoms, and finally add enough electrons to balance the charge on both sides of the equation. Be sure you see what has been done so you can do it on your own.

Step 1	Step 2	Step 3
Write the balanced half-reactions		**Add half-reactions**
$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	× 5	$5Fe^{2+} \rightarrow 5Fe^{+3} + \cancel{5e^-}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$MnO_4^- + 8\ H^+ + \cancel{5e^-} \rightarrow Mn^{2+} + 4\ H_2O$
Add equations together	**$MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4H_2O$**	

Example 3

$$HNO_3 + Cu + H^+ \rightarrow NO_2 + Cu^{2+} + H_2O \tag{1.3.5}$$

Solution

1. Determine what is oxidized, what is reduced, and write the two **balanced** half-reactions (Step 1)
2. Balance for electrons lost = electrons gained (Step 2)
3. Add equations together

Step 1	Step 2	Step 3
Write the balanced half-reactions		**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2e^-}$
$HNO_3 + H^+ + 1\ e^- \rightarrow NO_2 + H_2O$	× 2	$2HNO_3 + 2H^+ + \cancel{2e^-} \rightarrow 2NO_2 + 2H_2O$
Add equations together		**$2HNO_3 + Cu + 2H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O$**

When balancing redox reactions, either the oxidation number method or the half-reaction method may be used. Often you'll find that one method works best for some equations, while the other method is more suited for other reactions. Or you may find one method just easier to use. The practice exercises and assignments tell you which method to use for a reaction, but as you get get more experience you'll be able to make your own decision as to which method to use.

Writing half-reactions, however, is a skill you will need for our final topic in this course - Electrochemistry - so be sure you can write balanced half-reactions.

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1.4: The Activity Series- Predicting Spontaneous Redox Reactions

Learning Objectives

- Use the activity series to predict if a reaction will occur.

We see below two metals that can be exposed to water. The picture on the left is of sodium, which gives a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels.



Figure **1.4.1**: On the left, sodium reacts with water. On the right, silver in the form of cups do not react with water.

The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivities. The **activity series** is a list of elements in decreasing order of their reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table below is an activity series of most common metals and of the halogens.

Table **1.4.1**: Activity Series of Metals in Aqueous Solutions

most active (easily oxidized – readily lose electrons))		
lithium	Li	These metals displace hydrogen from water $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_2 + H_{2\ (g)}$ These elements are very reactive and react readily to form compounds
potassium	K	
barium	Ba	
calcium	Ca	
sodium	Na	
magnesium	Mg	These metals displace hydrogen from acids $Zn_{(s)} + HCl_{(aq)} \rightarrow ZnCl_2 + H_{2(g)}$
aluminum	A	
zinc	Zn	
chromium	Cr	
iron	Fe	
cadmium	Cd	
nickel	Ni	
tin	Sn	
lead	Pb	
hydrogen	H	
copper	Cu	These metals do not displace hydrogen from acids or water These elements are more stable, and form compounds less readily than do those higher in the table.
silver	Ag	
mercury	Hg	
platinum	Pt	
gold	Au	
least active		

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\mathrm{Ni}\,(s) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow \mathrm{Ni(NO_3)_2}\,(aq) + \mathrm{Pb}\,(s) \tag{1.4.1}$$

$$\mathrm{Ni}\,(s) + \mathrm{Fe(NO_3)_3}\,(aq) \rightarrow \mathrm{NR\ (no\ reaction)} \tag{1.4.2}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.

Steps for Problem Solving	**Example 1.4.1** Use the activity series to predict if the reaction below will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation. $\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$	**Example 1.4.2** Use the activity series to predict if the reaction below will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation. $\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$
Plan the problem.	Compare the placements of aluminum (the element doing the replacing) and zinc (the element being replaced) on the activity series.	Compare the placements of silver (the element doing the replacing) and hydrogen (the element being replaced) on the activity series.
Solve	Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathrm{Al(NO_3)_3}$. The balanced equation is: $$2\mathrm{Al}\,(s) + 3\mathrm{Zn(NO_3)_2}\,(aq) \rightarrow 2\mathrm{Al(NO_3)_3}\,(aq) + 3\mathrm{Zn}\,(s) \quad (1.4.3)$$	Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid. $$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow \mathrm{NR} \quad (1.4.4)$$

Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the series.

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1.5: Corrosion- Undesirable Redox Reactions

Corrosion of metals is a serious economic problem. Corrosion occurs as a result of spontaneous electrochemical reaction as metal undergoes oxidation. For example, the rusting of iron begins with the oxidation of solid iron:

$$\mathrm{Fe\,(s) \longrightarrow Fe^{2+}\,(aq) + 2\,e^-}$$

The corresponding reduction reaction involves water:

$$\mathrm{H_2O\,(l) + \tfrac{1}{2}\,O_2\,(g) + 2\,e^- \longrightarrow 2\,OH^-\,(aq)}$$

The flaky brown solid that we call rust forms when Fe^{2+} undergoes additional oxidation to form Fe^{3+}, then reacts with hydroxide ions to form iron (III) oxide, Fe_2O_3, and iron (III) hydroxide, $Fe(OH)_3$.

The rate of corrosion can be affected by several factors. Some examples:

- Metals corrode faster when in contact with another metal. The Statue of Liberty, for example, has a skin made of copper, but is supported by iron ribs. Since iron is oxidized more readily than copper, it acts as the anode. Earlier repairs to strengthen the statue used iron bolts, which exacerbated the problem. More recent repairs have replaced the iron ribs with stainless steel alloys. Stainless steel resists corrosion.
- Salt water speeds up the corrosion process, because the ions in salt water form a salt bridge between the anodic and cathodic sites. Salt may be great for icy roads, but it is tough on cars.

There are a number of ways to slow down corrosion, if not prevent it:

- Prevent oxygen and water from contacting the metal. This can be accomplished by paint, grease, plastic, or other methods of covering the metal.
- Cathodic protection: pieces of zinc or magnesium metal may be bolted to the surface of iron. Because they are more readily oxidized than Fe, Zn and Mg become oxidized over time, thus sparing and protecting the iron. Propeller shafts of speedboats are often protected this way. Anode rods in water heaters also work this way (they are often called **sacrificial anodes**). Galvanized nails—nails coated with the more reactive zinc—provide yet another example.
- Metal alloys: an alloy is a mixture of metals, or a mixture of a nonmetal with a metal. An alloy such as stainless steel (chromium is added to steel—a mixture of iron and other elements such as carbon—to make stainless steel) is highly resistant to corrosion, but can be prohibitively expensive.

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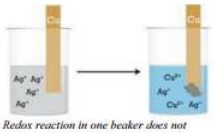
1.6: Batteries- Using Chemistry to Generate Electricity

Learning Objectives

- Identify the anode and the cathode given a diagram of an electrochemical cell
- Describe how batteries can produce electrical energy.

Electricity is an important form of energy that you use every day. It runs your calculators, cell phones, dishwashers, and watches. This form of energy involves moving electrons through a wire and using the energy of these electrons. Electrochemical cells used for power generation are called batteries. Although batteries come in many different shapes and sizes, there are a few basic types. You won't be required to remember details of the batteries, but some general information and features of each type are presented here. Many important chemical reactions involve the exchange of one or more electrons, and we can use this movement of electrons as electricity; batteries are one way of producing this type of energy. The reactions that drive electricity are called oxidation-reduction (or "redox") reactions.

Batteries



Redox reaction in one beaker does not produce electricity. (Source: Richard Parsons. CC-BY-SA)

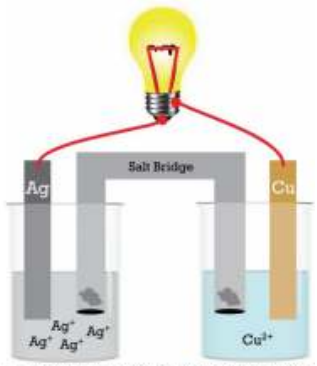
Batteries are devices that use chemical reactions to produce electrical energy. These reactions occur because the products contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur, but also often gives off energy to the surroundings. Some of these reactions can be physically arranged so that the energy given off is in the form of an electric current. These are the type of reactions that occur inside batteries. When a reaction is arranged to produce an electric current as it runs, the arrangement is called an **electrochemical cell,** a **Voltaic Cell,** or a **Galvanic Cell.**

If a strip of copper is placed in a solution of silver nitrate, the following reaction takes place:

$$2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq) \tag{1.6.1}$$

In this reaction, copper atoms are donating electrons to silver ions, so the silver ions are reduced to silver atoms and copper atoms are oxidized to copper (II) ions.

As the reaction occurs, an observer would see the solution slowly turn blue (Cu^{2+} ions are blue in solution) and a mass of solid silver atoms would build up on the copper strip.



In a battery, the oxidation and reduction half-reactions occur in separate containers, allowing the electrons to flow through a wire producing electricity.

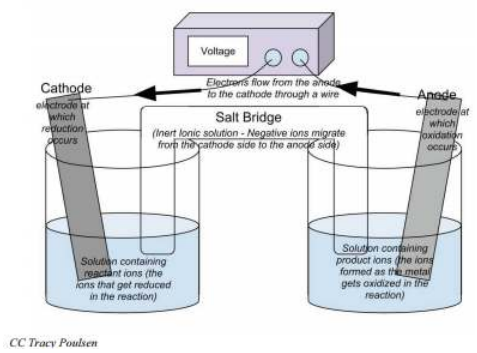
The reaction we just described is not set up in such a way as to produce electricity. It is true that electrons are being transferred, but to produce electricity, we need electrons flowing through a wire so that we can use the energy of these electrons. This reaction, $2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$, is one that could be arranged to produce electricity. To do this, the two half-reactions (oxidation and reduction) must occur in separate compartments, and the separate compartments must remain in contact through a **salt bridge** (an ionic solution) and an **external wire**.

In this electrochemical cell, the copper metal must be separated from the silver ions to avoid a direct reaction. Each electrode in its solution could be represented by a half-reaction.

$$Cu \rightarrow Cu^{2+} + 2e^{-} \tag{1.6.2}$$

$$2Ag^{+} + 2e^{-} \rightarrow 2Ag \tag{1.6.3}$$

The wire connects the two halves of the reaction, allowing electrons to flow from one metal strip to the other. In this particular example, electrons will flow from the copper electrode (which is losing electrons) into the silver electrode (which is where the silver ions gain the electrons). The cell produces electricity through the wire and will continue to do so as long as there are sufficient reactants (Ag^{+} and Cu) to continue the reaction.



Electrochemical cells will always have two electrodes—the pieces of metal where electrons are gained or lost. (In this example, the strip of Ag metal and Cu metal are the electrodes.) The electrode where **reduction** occurs and electrons are gained is called the **cathode**. The electrode where **oxidation** occurs and electrons are lost is called the **anode**. Electrons will always move from the anode to the cathode. The electrons that pass through the external circuit can do useful work such as lighting lights, running cell phones, and so forth.

If the light bulb is removed from the circuit with the electrochemical cell and replaced with a voltmeter, the voltmeter will measure the cell voltage or electromotive force (E_{cell} or EMF) of the combination of half-cells. The size of the voltage produced by a cell depends on the temperature, the metals used for electrodes, and the concentrations of the ions in the solutions. For this particular cell, if the concentration of solutions is 1 M and the temperature is 25ºC, the initial measured voltage is 0.460 Volts. However, as the redox reaction progresses, the voltage will decrease and it becomes 0 Volts when the reactants are totally consumed. In this case, we say that the battery is dead.

It may seem complicated to construct an electrochemical cell due to all of their complexities. Electrochemical cells are actually easy to make and sometimes even occur accidentally. If you take two coins of different denomination, push them part way through the peel of a whole lemon, and then connect the two coins with a wire, a small electric current will flow.

This type of battery is known as a **wet cell battery** since it involves electrolytes in solution. Wet cells were the first known type of electrochemical cell to generate electricity. However, their application is limited since wet cells are prompted to leak problems. Most modern applications of electrochemical batteries involve dry cells. In a **dry cell**, electrolytes are used as a paste rather than as a liquid, so there less likely to leak. Batteries may be classified as primary cells (non-rechargeable) or secondary cells (rechargeable)

Some modern type of batteries are listed below:

1. Dry Cell Batteries

- Non-rechargeable (primary battery)
- Electrolytes are present as a paste rather than as a liquid.
- General purpose battery used for flashlights, transistor radios, toys, etc.
- The basic dry cell battery consists of: zinc case as the anode (oxidation); a graphite rod as the cathode (reduction) surrounded by a moist paste of either MnO_2, NH_4Cl, and $ZnCl_2$ (or, in alkaline dry cells, a KOH electrolytic paste).
- General reactions for the battery: manganese (IV) oxide-zinc cell (different batteries have different reactions—you don't need to remember any of these reactions).

cathode	$2MnO_{2(s)} + 2\ NH_4^+{}_{(aq)} + 2e^- \rightarrow Mn_2O_{3\ (s)} + H_2O_{(l)} + 2NH_{3\ (aq)}$
anode	$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

- - Maximum voltage of 1.5V. By connecting several cells in a series, 90V can be achieved.
  - Advantages of alkaline batteries: consistent voltage, increased capacity, longer shelf life, and reliable operation at temperatures as low as -40°C.
  - Disadvantage: higher cost.

2. Storage Batteries

- Rechargeable (secondary batteries)
- An example: the lead-acid battery used in cars. The anode is a grid of lead-antimony or lead-calcium alloy packed with spongy lead; the cathode is lead (IV) oxide. The electrolyte is aqueous sulfuric acid. This battery consists of numerous small cells connected in parallels (anode to anode; cathode to cathode).
- General reaction:

cathode	$PbO_{2(s)} + 4H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4\,(s)} + 2H_2O_{(l)} + 2NH_{3\,(aq)}$
anode	$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4\,(s)} + 2e^-$

- - Secondary batteries are recharged by passing a current through the battery in the opposite direction. In a car battery, this occurs when the engine is running.
  - Other examples include the nickel-iron alkaline battery, nickel-zinc battery, nickel-cadmium alkaline battery, silver-zinc battery, and silver-cadmium battery.

3. Fuel Cells

- Fuel cells are electrochemical cells that convert the energy of a redox combustion reaction directly into electrical energy. Fuel cells require a continuous supply of reactants and a constant removal of products.
- The cathode reactant is usually air or pure oxygen; the anode fuel is a gas such as hydrogen, methane, or propane. Carbon electrodes typically contain a catalyst. The electrolyte is typically KOH.
- General reaction:

cathode	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$
anode	$2H_{2\,(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
net	$2H_{2\,(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

- - Advantages: no toxic waste products (water is the only product); very efficient energy conversion (70-80% efficient).
  - Disadvantage: too expensive for large-scale use.

Summary

- A reaction in which there is a transfer of electrons is said to be an oxidation-reduction reaction, or a redox reaction.
- A substance that loses electrons is said to be oxidized, and the substance that gains electrons is said to be reduced.
- Redox reactions can be used in electrochemical cells to produce electricity.
- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode, and the electrode where reduction occurs is called the cathode.

Vocabulary

- **Electrochemical cell** - An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (a battery).
- **Electrolysis** - A chemical reaction brought about by an electric current.
- **Electroplating** - A process in which electrolysis is used as a means of coating an object with a layer of metal.

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- Wikipedia contributors. (2021, May 11). Electric battery. In *Wikipedia, The Free Encyclopedia*. Retrieved 13:37, May 21, 2021, from https://en.wikipedia.org/w/index.php?title=Electric_battery&oldid=1022586423

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1.7: Standard Reduction Potentials and Batteries

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

Using batteries to measure the tendency of elements to undergo oxidation or reduction

The cell potential results from the difference in the tendency of certain redox pairs at each electrode to be reduced or oxidized. While it is impossible to quantitatively measure that tendency in terms of absolute values, we can assign an electrode the value of zero and then use it as a reference (**standard electrode**). Therefore, we can compare any other electrode to that standard electrode by building a battery, and measure the tendency of each electrode to be reduced in units of volts (**standard potential *E°***) compared to the standard electrode. This is similar to measuring the elevation of a mountain by considering the sea level as the zero point in altitude.

The electrode chosen as the zero voltage (standard electrode) is shown in Figure 17.4.1 and is called the **standard hydrogen electrode** (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,H^+(aq,\,1\,M)+2\,e^- \rightleftharpoons H_2(g,\,1\,atm) \quad E°= 0\,V \tag{1.7.1}$$

***E*° is the standard reduction potential**. The superscript "°" on the *E* denotes standard conditions (1 bar or 1 atm for gases, 1 *M* for solutes). The voltage is defined as zero for all temperatures.

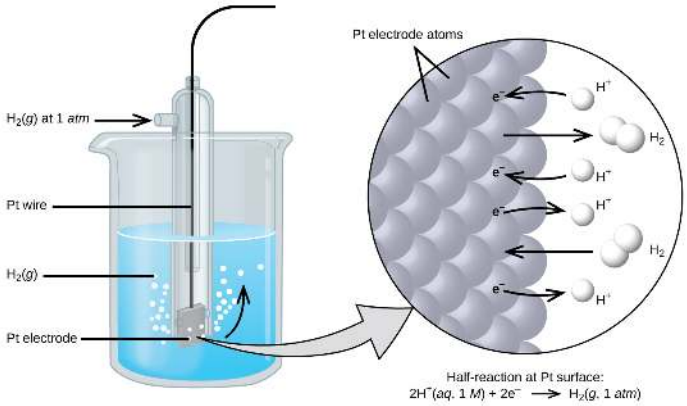


Figure **1.7.1**: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure **1.7.2**). In cell notation, the reaction is

$$Pt(s)\,|\,H_2(g,\,1\,atm)\,|\,H^+(aq,\,1\,M)\,\|\,Cu^{2+}(aq,\,1\,M)\,|\,Cu(s) \tag{1.7.2}$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): } H_2(g) \longrightarrow 2\,H^+(aq)+2\,e^-\\&\text{Cathode (reduction): } Cu^{2+}(aq)+2\,e^- \longrightarrow Cu(s)\\&\text{Overall: } Cu^{2+}(aq)+H_2(g) \longrightarrow 2\,H^+(aq)+Cu(s)\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{1.7.3}$$

$$+0.34\,V = E°_{Cu^{2+}/Cu} - E°_{H^+/H_2} = E°_{Cu^{2+}/Cu} - 0 = E°_{Cu^{2+}/Cu} \tag{1.7.4}$$

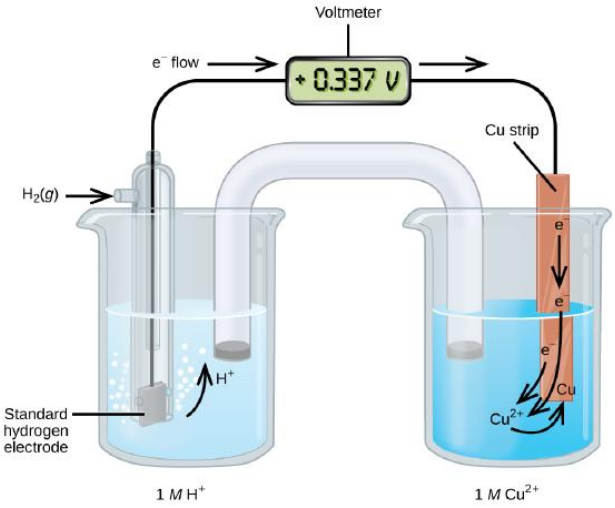


Figure **1.7.2**: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure **1.7.2**, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s) \tag{1.7.5}$$

Electrons flow from left to right, and the reactions are

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

The **standard cell potential** (E^ocell) can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \tag{1.7.6}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}} \tag{1.7.7}$$

It is important to note that the potential is *not* doubled for the cathode reaction, even though a "2" stoichiometric coefficient is needed to balance the number of electrons exchanged. Also, **the standard cell potential (E^ocell) for a battery has always a positive value, that is, E^ocell > 0 volts**. That is because the redox reaction between the electrodes is spontaneous, and the electrons will circulate spontaneously according to the tendency of each electrode to be reduced or oxidized. By convention, we always compare the tendency of a particular electrode to be reduced, that is, we look at its standard reduction potential.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s) \tag{1.7.8}$$

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V} \tag{1.7.9}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table **1.7.1**. A more complete list is provided in Tables P1 or P2.

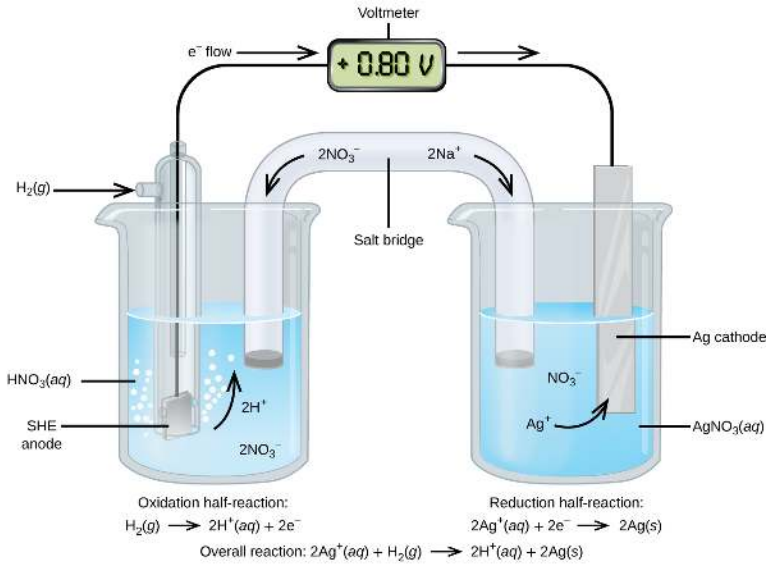


Figure **1.7.3**: A galvanic cell can be used to determine the standard reduction potential of Ag^{+}. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table **1.7.1**: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$F_2(g)+2\,e^- \longrightarrow 2\,F^-(aq)$	+2.866
$PbO_2(s)+SO_4{}^{2-}(aq)+4\,H^+(aq)+2\,e^- \longrightarrow PbSO_4(s)+2\,H_2O(l)$	+1.69
$MnO_4{}^-(aq)+8\,H^+(aq)+5\,e^- \longrightarrow Mn^{2+}(aq)+4\,H_2O(l)$	+1.507
$Au^{3+}(aq)+3\,e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g)+2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.35827
$O_2(g)+4\,H^+(aq)+4\,e^- \longrightarrow 2\,H_2O(l)$	+1.229
$Pt^{2+}(aq)+2\,e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq)+2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.0873
$Ag^+(aq)+e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2{}^{2+}(aq)+2\,e^- \longrightarrow 2\,Hg(l)$	+0.7973
$Fe^{3+}(aq)+e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4{}^-(aq)+2\,H_2O(l)+3\,e^- \longrightarrow MnO_2(s)+4\,OH^-(aq)$	+0.558
$I_2(s)+2\,e^- \longrightarrow 2\,I^-(aq)$	+0.5355
$NiO_2(s)+2\,H_2O(l)+2\,e^- \longrightarrow Ni(OH)_2(s)+2\,OH^-(aq)$	+0.49
$Cu^{2+}(aq)+2\,e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s)+2\,e^- \longrightarrow 2\,Hg(l)+2\,Cl^-(aq)$	+0.26808
$AgCl(s)+e^- \longrightarrow Ag(s)+Cl^-(aq)$	+0.22233
$Sn^{4+}(aq)+2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2\,H^+(aq)+2\,e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq)+2\,e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq)+2\,e^- \longrightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq)+2\,e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq)+2\,e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s)+2\,e^- \longrightarrow Pb(s)+SO_4{}^{2-}(aq)$	−0.3505
$Cd^{2+}(aq)+2\,e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq)+2\,e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq)+3\,e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq)+2\,e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s)+2\,e^- \longrightarrow Zn(s)+2\,OH^-(aq)$	−1.245
$Zn^{2+}(aq)+2\,e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq)+3\,e^- \longrightarrow Al(s)$	−1.662
$Mg^{2+}(aq)+2\,e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq)+e^- \longrightarrow Na(s)$	−2.71

Half-Reaction	E° (V)
$Ca^{2+}(aq)+2\,e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq)+2\,e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq)+e^- \longrightarrow K(s)$	−2.931
$Li^+(aq)+e^- \longrightarrow Li(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions. **The higher the standard reduction potential, the higher the tendency of that electrode to be reduced**. All electrodes with a positive standard reduction potential value have a higher tendency than hydrogen to be reduced, while all electrodes with a negative standard reduction potential have less tendency than hydrogen to be reduced.

Since the standard reduction potential is a measure of a particular electrode (redox couple) to be reduced, we can use this value to determine which electrode will be the cathode and which electrode will be anode when building an electrochemical cell using two electrodes listed on the table above. We can also use the standard reduction potential of each electrode to calculate the resulting standard cell potential (E^ocell). See the following example:

Example 1.7.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the cathode and anode.

Solution

Using Table **1.7.1**, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq)+3\,e^- \longrightarrow Au(s) \quad E^\circ_{Au^{3+}/Au} = +1.498\ V \tag{1.7.10}$$

$$Ni^{2+}(aq)+2\,e^- \longrightarrow Ni(s) \quad E^\circ_{Ni^{2+}/Ni} = -0.257\ V \tag{1.7.11}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } Ni(s) \longrightarrow Ni^{2+}(aq)+2\,e^- \quad E^\circ_{anode} = E^\circ_{Ni^{2+}/Ni} = -0.257\ V$$
$$\text{Cathode (reduction): } Au^{3+}(aq)+3\,e^- \longrightarrow Au(s) \quad E^\circ_{cathode} = E^\circ_{Au^{3+}/Au} = +1.498\ V$$

The least common factor is six, so the overall reaction is

$$3\,Ni(s)+2\,Au^{3+}(aq) \longrightarrow 3\,Ni^{2+}(aq) + 2\,Au(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.498\ V - (-0.257\ V) = 1.755\ V \tag{1.7.12}$$

From the half-reactions, Ni is oxidized, so it is the anode (or the reducing agent), and Au^{3+} is reduced, so it is the cathode (or the oxidizing agent). The resulting standard cell potential (E^ocell) is 1.755 V. As expected, this value is positive since we are working with a galvanic or electrochemical cell.

Exercise 1.7.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$\mathrm{Mg}(s) + 2\,\mathrm{Ag}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{Ag}(s) \quad E^\circ_{\text{cell}} = 0.7996\ \mathrm{V} - (-2.372\ \mathrm{V}) = 3.172\ \mathrm{V}$$

Contributors and Attributions

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, $E°$, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential ($E°$)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Contributors and Attributions

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1.8: Cell Notation and Conventions

Rather than drawing a complete diagram like the figures in the Galvanic Cells section, it is convenient to specify a galvanic cell in shorthand form. The two cells we have just described would be written as

$$\mathrm{Zn \mid Zn^{2+}(1\,M) \parallel Cu^{2+}(1\,M) \mid Cu} \tag{1.8.1}$$

and

$$\mathrm{Pt,\ Cl_2\,(g) \mid Cl^-(1\,M) \parallel Fe^{2+}(1\,M),\ Fe^{3+}(1\,M) \mid Pt} \tag{1.8.2}$$

The components of the cell are written in order, starting with the left-hand and moving across the salt bridge to the right. A single vertical line indicates a phase boundary, such as that between the solid Zn electrode and $Zn^{2+}(aq)$, or between $Cl_2(g)$ and $Cl^-(aq)$. The double vertical line represents a salt bridge. Spectator ions, like $SO_4^{2-}(aq)$ in the Zn–Cu cell, are usually omitted.

By convention, the electrode written to the *left* of the salt bridge in this cell notation is always taken to be the *anode*, and the associated half-equation is always written as an *oxidation*. The right-hand electrode is therefore always the *cathode*, and the half-equation is always written as a *reduction*. This is easy to remember, because reading from left to right gives anode and cathode in alphabetical order. The **cell reaction** corresponding to a given shorthand description is obtained by summing the half-equations after multiplying by any factors necessary to equalize the number of electrons lost at the anode with the number gained at the cathode. Unless otherwise stated, standard conditions of 1 *M* are usually implied. However, non-standard cells can be created.

Example 1.8.1 : Half Reactions

Write the half-equations and cell reactions for each of the following cells:

a. $\mathrm{Ag \mid Ag^+ \parallel H^+ \mid H_2 \mid Pt}$
b. $\mathrm{Pt \mid Cr_2O_7^{2-},\ Cr^{3+},\ H^+ \parallel Br^- \mid Br_2\,(l) \mid Pt}$

Solution

a) Since the half-equation at the left electrode is taken by convention to be oxidation, we have

$$\mathrm{Ag \rightarrow Ag^+ + e^-} \tag{1.8.3}$$

At the right-hand electrode, then, we must have a reduction:

$$\mathrm{2\,H^+ + 2e^- \rightarrow H_2} \tag{1.8.4}$$

Multiplying the first half-equation by 2 and summing gives the cell reaction

$$\mathrm{2\,Ag + 2\,H^+ \rightarrow 2\,Ag^+ + H_2\,(g)} \tag{1.8.5}$$

b) Following the same procedure as in part a, we obtain

$$\mathrm{2\,Cr^{3+} + 7\,H_2O \rightarrow Cr_2O_7^{2-} + 14\,H^+ + 6e^-} \tag{1.8.6}$$

Left electrode

$\mathrm{(Br_2\,(l) + 2e^- \rightarrow 2\,Br^-) \cdot 3}$ Right electrode

$$\mathrm{2\,Cr^{3+} + 7\,H_2O + 3\,Br_2\,(l) \rightarrow Cr_2O_7^{2-} + 14\,H^+ + 6\,Br^-} \tag{1.8.7}$$

Cell reaction

Note: The procedures described in other sections for balancing redox equations were used in arriving at the above results.

Example 1.8.2: Galvanic Cell

Describe in shorthand notation a galvanic cell for which the cell reaction is

$$\mathrm{Cu\,(s) + 2\,Fe^{3+}\,(aq) \rightarrow Cu^{2+}\,(aq) + 2\,Fe^{2+}\,(aq)} \tag{1.8.8}$$

Solution

First divide the cell reaction into half-equations:

- Oxidation: $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2e^-$
- Reduction: $\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$

Then write the oxidation as the left-hand electrode and the reduction on the right:

$$\mathrm{Cu \mid Cu^{2+} \parallel Fe^{2+}, Fe^{3+} \mid Pt} \tag{1.8.9}$$

(Since both Fe^{2+} and Fe^{3+} are in solution, a Pt electrode is used.)

The conventions we have developed can be used to decide whether the cell reaction is actually spontaneous. If it is, an oxidation will release electrons to the external circuit at the left-hand electrode. If a voltmeter is placed in the circuit, these electrons will make its left-hand terminal negative. Since the right-hand electrode corresponds to reduction, electrons will be withdrawn from the right-hand terminal of the voltmeter. This is shown for the Zn–Cu cell in Figure 1 from the Galvanic Cells section. You can readily confirm that the spontaneous cell reaction (Eq. (1) from Galvanic Cells) corresponds to the shorthand cell notation of Eq. 1.8.1.

For the cell shown in Figure 1 in Galvanic Cells, the shorthand notation is

$$\mathrm{Pt, Cl_2(g) \mid Cl^-(1\,M) \parallel Fe^{2+}(1\,M), Fe^{3+}(1\,M) \mid Pt} \tag{1.8.10}$$

According to the conventions we have just developed, this corresponds to the cell reaction

$$\mathrm{2\,Cl^-(aq) + 2\,Fe^{3+}(aq) \rightarrow Cl_2(g) + 2\,Fe^{2+}(aq)} \tag{1.8.11}$$

But this is the of the spontaneous cell reaction we described before (Eq. (2) from Galvanic Cells). Since the cell reaction is nonspontaneous, electrons will not be forced into the external circuit at the left-hand electrode, and they will not be withdrawn at the right. In fact the reverse will actually occur. Thus if a voltmeter is connected to this cell, its right-hand terminal will become more negative and its left-hand terminal will become more positive.

In general, if a galvanic cell is connected to a voltmeter, the electrode connected to the negative terminal of the meter must be the anode. If our shorthand cell notation shows that electrode on the left, then the corresponding cell reaction must be spontaneous. Electrons will be released by the oxidation half-equation on the left and accepted by the reduction on the right. If, on the other hand, the voltmeter shows that the right-hand electrode is releasing electrons, then we must have written our shorthand notation *backwards*. This means that the reverse of the cell reaction obtained by our rules must actually be occurring, and it is that reverse reaction which is spontaneous. Thus by simply observing which electrode in the cell releases electrons and which accepts them, that is, by finding which electrode is negative and which positive, we can determine whether the cell reaction is spontaneous.

Contributors and Attributions

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1.9: Cells at Non-Standard Conditions

As shown in the section on cell notation, a galvanic cell in shorthand form can be written:

$$\mathrm{Zn}\,|\,\mathrm{Zn^{2+}}\ (1M)\ \|\ \mathrm{Cu^{2+}}\ \ (1M)\,|\,\mathrm{Cu} \tag{1.9.1}$$

The parenthetical notes of (1 *M*) are frequently omitted because 1 *M* is at the standard state. However, cells can be created which use concentrations other than 1 *M*. In such a case, one must always indicate the concentrations as shown above. In fact, as the reaction for the cell written above takes place (that is, as the cell provides electric current), Cu^{2+} will be used up while Zn^{2+} will be generated. The reactant concentrations will decrease and the product concentrations will increase until the solution has reached a state of equilibrium. These equilibrium concentrations are not likely to be at the standard 1 *M* solutions indicated above.

The voltage of a cell at non-standard state is modified by the relative concentrations of the reactants and products, indicated as []. The equation for the reaction in the cell is

$$\mathrm{Zn} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Cu} + \mathrm{Zn^{2+}} \tag{1.9.2}$$

To calculate the electromotive force of a non-standard galvanic cell we use **The Nernst Equation**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n}\log\,[products]/[reactants] \tag{1.9.3}$$

(T = 298 \text{ K})\]

This equation is valid at 298ºK, which the temperature at which most of the Galvanic cells are used. Only the soluble species (or gases) affect the cell potential, **not the solid electrode**. The n value refers to the number of electrons exchanged (in our reaction above, n=2). If you calculate the [product]/[reactants] ratio for the standard-state concentration of 1 *M*, note how the second term on the right-hand-side disappears and you recover $E_{\text{cell}} = E^{\circ}_{\text{cell}}$.

This expression for the Nernst equation is a simplified version that applies only when the number of electrons gained at the anode is identical to the number of electrons lost at the cathode. In other words, this expression for the Nernst equation is only valid when multiplication is not necessary to balance the number of electrons in the overall cell reaction. When the number of electrons involved at the cathode and anode is not the same, the expression is more complicated and it involves the concept of reaction quotient (Q), which we will learn later in the semester.

Example 1.9.1 : Voltage of a Galvanic Cell

Determine the voltage measured for this galvanic cell. You may need to use the Table of Standard Reduction Potentials.

$$\mathrm{Cu^{+}}(aq)(1M)\,|\,\mathrm{Cu}\,\|\,\mathrm{Ag}\,|\,\mathrm{Ag^{+}}(0.8M)$$

Solution:

The strategy for solving these problems is to first find the standard electromotive force, as shown in another section, and then write the balanced chemical equation, from which you can derive *reactants and products*. Remember that solids do not participate in the Nernst equation.

$$E^{\circ}_{\text{cell}} = 0.7991\ \mathrm{V} - (0.520)\ \mathrm{V} = 0.2791\ \mathrm{V}$$

$$\mathrm{Ag^{+}}(aq) + \mathrm{Cu(s)} \rightarrow \mathrm{Ag(s)} + \mathrm{Cu^{+}}(aq)$$

The expression for [products]/[reactants] can be derived only from the balanced overall cell reaction. Thus, using the Nernst Equation, we have,

$$
\begin{aligned}
E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592\ \text{V}}{z} \log Q \\
&= 0.2791\ \text{V} - \frac{0.0592\ \text{V}}{1} \log \frac{\{\text{Cu}^{+}(aq)\}}{\{\text{Ag}^{+}(aq)\}} \\
&= 0.2791\ \text{V} - \frac{0.0592\ \text{V}}{1} \log \frac{(1\ M)}{(0.8\ M)} \\
E_{\text{cell}} &= 0.2734\ \text{V}
\end{aligned}
$$

Attributions

Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, E. V., John W., & Hahn, A. (2020, November 5). Cells at Non-Standard Conditions. Chemical Education Digital Library (ChemEd DL). https://chem.libretexts.org/@go/page/49575

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1.10: Electrolysis- Using Electricity to Do Chemistry

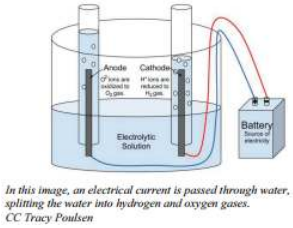
So far, we have discussed how electricity can be produced from chemical reactions in batteries. In this type of electrochemical or galvanic cells, a spontaneous reaction occurs, and the electrons flow from the anode towards the cathode, resulting in a positive cell potential (E^ocell >0). In other words, a chemical reaction is used to produce electrical work (like powering a light bulb).

However, the opposite is also possible. We can use electrical energy to power a non-spontaneous chemical reaction within an electrochemical cell. This type of cell is called an **electrolytic cell**. In an electrolytic cell, the electron are forced to circulate in the opposite direction determined by the standard reduction potentials, and the resulting cell potential has a negative value (E^ocell <0). In other words, in an electrochemical cell, a spontaneous redox reaction is used to create an electric current; in an electrolytic cell, the reverse will occur—an electric current will be required in order to cause a non-spontaneous chemical reaction to occur.

	Electrochemical Cells	Electrolytic Cells
Energy conversion	Chemical → Electrical	Electrical → Chemical
Spontaneous chemical reaction?	Yes	No
Value of E°	Positive	Negative

These electrolytic have many uses. For example, electrolysis is a process that involves forcing electricity through a liquid or solution to cause a reaction to occur. Electrolysis reactions will not run unless energy is put into the system from outside. In the case of electrolysis reactions, the energy is provided by the battery. Think of electrolysis and electrolytic cells as the opposite of electrochemical cell. We will look at three examples of the electrolytic process, keeping our discussion on a very basic level—the electrolysis of molten sodium chloride, the electrolysis of water, and electroplating.

Electroplating



In this image, an electrical current is passed through water, splitting the water into hydrogen and oxygen gases. CC Tracy Poulsen

Figure 16.7.1: An electrical current is passed through water, splitting the water into hydrogen and oxygen gases.

If electrodes connected to battery terminals are placed in liquid sodium chloride, the sodium ions will migrate toward the negative electrode and be reduced while the chloride ions migrate toward the positive electrode and are oxidized. The processes that occur at the electrodes can be represented by what are called half-equations.

Reduction occurs at the positive electrode:

$$\mathrm{Na^+ + e^- \rightarrow Na} \tag{1.10.1}$$

Oxidation occurs at the negative electrode:

$$\mathrm{2Cl^- \rightarrow Cl_2 + 2e^-} \tag{1.10.2}$$

The overall reaction for this reaction is:

$$\mathrm{2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2} \tag{1.10.3}$$

With appropriate treatment from the battery, it is possible to get the metal being reduced in an electrolysis process to adhere strongly to the electrode. The use of electrolysis to coat one material with a layer of metal is called **electroplating**. Usually, electroplating is used to cover a cheap metal with a layer of more expensive and more attractive metal. Many people buy jewelry

that is plated in gold. Sometimes, electroplating is used to get a surface metal that is a better conductor of electricity. When you wish to have the surface properties of gold (attractive, corrosion resistant, or good conductor), but you don't want to have the great cost of making an entire object out of solid gold, the answer may be to use cheap metal to make the object and then electroplate a thin layer of gold on the surface.

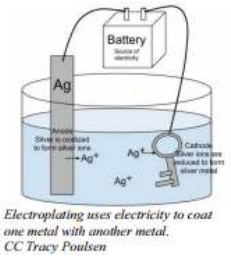


Figure 16.7.2: Silver plating.

To silver plate an object like a spoon (plated silverware is less expensive than pure silver), the spoon is placed in the position of the cathode in an electrolysis set up with a solution of silver nitrate. When the current is turned on, the silver ions will migrate through the solution, touch the cathode (spoon) and adhere to it. With enough time and care, a layer of silver can be plated over the entire spoon. The anode for this operation would often be a large piece of silver, from which silver ions would be oxidized and these ions would enter the solution. This is a way of ensuring a steady supply of silver ions for the plating process.

- Half-reaction at the cathode:

$$\mathbf{Ag^+ + e^- \rightarrow Ag} \tag{1.10.4}$$

- Half-reaction at the anode:

$$\mathbf{Ag \rightarrow Ag^+ + e^-} \tag{1.10.5}$$

Some percentage of the gold and silver jewelry sold is electroplated. The connection points in electric switches are often gold plated to improve electrical conductivity, and most of the chromium pieces on automobiles are chromium plated.

Electrolysis of Molten Sodium Chloride

If we look at the latin roots of the word "electrolysis" we learn that it means, essentially, to "break apart" (*lysis*) using electricity. Our first example of an electrolytic cell will examine how an electric current can be used to break apart an ionic compound into its elements. The following equation represents the breaking apart of $NaCl_{(l)}$:

$2NaCl_{(l)} \rightarrow 2Na_{(l)} + Cl_{2\,(g)}$

The half-reactions involved in this process are:

			E°
reduction	$2Na^+_{(l)} + 2e^- \rightarrow Na_{(s)}$		-2.71 V
oxidation	$Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2\,e^-$		-1.36V
	net voltage required		**- 4.07V**

Notice that a negative voltage (-4.07V) results when we add up the half-reactions. This tells us that the overall reaction will **NOT** be spontaneous, and a minimum of 4.07 volts will be required for this reaction to occur.

As we shall see, our set-up will have a number of similarities to our electrochemical cells. We will need electrodes and an electrolyte to carry the electric current.

In our NaCl example, the electrodes will simply carry the current, but otherwise will not be directly involved in the reaction. The electrolyte will be the actual molten (melted) NaCl. The electrodes and electrolyte are both required to carry the electric current.

Molten NaCl must be used because solid ionic compounds do not carry an electric charge.

Some key differences with an electrochemical cell set-up:

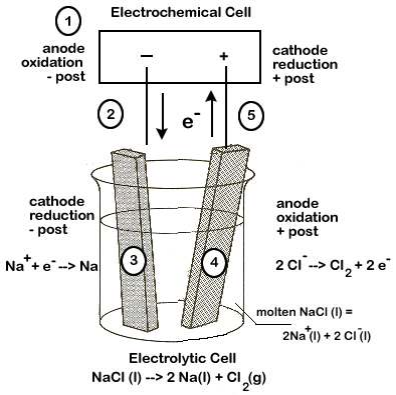
- The two half-reactions are not separated by a salt bridge.
- An electrochemical cell (or other source of electric current) will be required.

Other important items to note:

- The anode of the electrolytic cell is the site of oxidation and the cathode is the site of reduction, just as in an electrochemical cell.
- In an electrochemical cell, the anode is negative and cathode positive, but this is reversed in the electrolytic cell—the anode is positive and the cathode is negative.

Carefully study the diagram of our set up, taking special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

1. 1. Electrons are "produced" in the battery at the anode, the site of oxidation.
   2. The electrons leave the electrochemical cell through the external circuit.
   3. These negative electrons create a negative electrode in the electrolytic cell, which attracts the positive Na^+ ions in the electrolyte. Na^+ ions combine with the free electrons and become reduced ($2Na^+ + 2e^- \rightarrow Na$).
   4. Meanwhile, the negative Cl^- become attracted to the positive electrode of the electrolytic cell. At this electrode, chlorine is oxidized, releasing electrons ($Cl^- \rightarrow Cl_2 + 2\ e^-$).
   5. These electrons travel through the external circuit, returning to the electrochemical cell.



Electrolysis of Water

Our second example of electrolysis and electrolytic cells involves the breakdown of water. We will find a situation very similar to the electrolysis of molten NaCl. The following equation represents the breaking apart of $H_2O_{(l)}$:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\ (g)}$

It may be more difficult to predict the half-reactions involved, but they are:

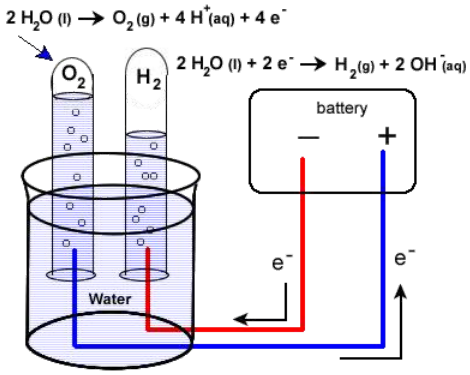
			E°
reduction	$2H_2O_{(l)} + 2e^- \rightarrow H_2 + 2\ OH^-$		-0.83 V
oxidation	$2H_2O_{(l)} \rightarrow O_2 + 4H^+ + 4e^-$		-1.23V
	(see note below for net equation)		
		net voltage required	**- 2.06V**

The set up will be very similar to our last example with some minor differences. Water does not carry a charge well, so an electrolyte is added to the water. Vinegar, a weak acid (acetic acid) may be used. To collect the hydrogen and oxygen gases produced, inverted test tubes are often added, as shown in our diagram below.

Again, take special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)}$

$2H_2O_{(l)} \rightarrow O_{2\ (g)} + 4H^+_{\ (aq)} + 4e^-$



1. 1. Electrons are "produced" in the battery at the anode, the site of oxidation.
   2. The electrons leave the electrochemical cell through the external circuit.
   3. These negative electrons create a negative electrode in the electrolytic cell which causes the reduction of water. Note that the area around this electrode will become basic as OH^- ions are produced.
   4. Meanwhile, the positive electrode water will undergo oxidation.
   5. Electrons produced during this oxidation process will return to the electrochemical cell.

A note about the balanced equation for the electrolysis of water:

You may notice from the half reactions that adding up the equations doesn't initially give us our net equation of:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\ (g)}$

Once you balance for electrons (multiply the reduction equation by 2), you'll find that the equations actually add up to:

$6H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\ (g)} + 4H^+_{\ (aq)} + 4\ OH^-_{(aq)}$

The hydrogen and hydroxide ions will combine to form 4 moles of $H_2O_{(l)}$. Finding our net amount of $H_2O_{(l)}$ involved gives us our final equation:

$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2\ (g)}$

Connections: Spontaneous and non-spontaneous reactions in nature

The fact the spontaneous reactions are capable of producing energy, while nonspontaneous reactions require energy to occur is closely related to what happens in nature.

During metabolism, glucose ($C_6H_{12}O_6$) is oxidized with oxygen in a spontaneous reaction that releases energy:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$

In this redox reaction, glucose is oxidized to CO_2 while oxygen is reduced. The reaction has a positive E^ocell, and 2870 kilojoules of energy are released for mole of metabolized glucose. The energy released by this spontaneous reaction is used by all living organism to grow, reproduce, move, etc. This reaction resembles a galvanic cell.

However, during photosynthesis, the opposite reaction takes place:

$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$

In this redox reaction, CO_2 is reduced to glucose, while water is oxidized to O_2. The reaction is non-spontaneous, so it resembles an electrolytic cell. The reaction requires energy (2870 kilojoules per mole of glucose formed). Where does the energy for this electrolytic reaction come from? As you might guess, the energy comes from the sun.

Summary

- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode and the electrode where reduction occurs is called the cathode.
- In electroplating, the object to be plated is made the cathode.

Vocabulary

- **Electrochemical cell** - An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (also known as a battery).
- **Electrolysis** - A chemical reaction brought about by an electric current.
- **Electroplating** - A process in which electrolysis is used as a means of coating an object with a layer of metal.

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CHAPTER OVERVIEW

2: The States of Matter

2.1: States of Matter
2.2: Kinetic-Molecular Theory
2.3: Gas Laws
2.4: Diffusion and Effusion- Graham's Law
2.5: Changes in State and Heating Curves

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2.1: States of Matter

Learning Outcomes

- List the three states of matter and give examples of each.
- Describe the properties of each state of matter.
- Identify and describe each type of change in state.
- Recognize that boiling and melting points vary with each substance.
- Recognize that a substance's boiling point depends on the pressure.

States of Matter

Another way that we can describe the properties of matter is the state (also called phase). The amount of energy in molecules of matter determines the **state of matter**. Matter can exist in one of several different states, including a gas, liquid, or solid state. These different states of matter have different properties, which are illustrated in the figure below.

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide. Forces between atoms or molecules are not strong enough to hold them together.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another. Forces between atoms or molecules are strong enough to keep the molecules relatively close together but not strong enough to prevent them from moving past one another.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another. Forces between atoms or molecules are strong enough to keep the molecules together and to prevent them from moving past one another.

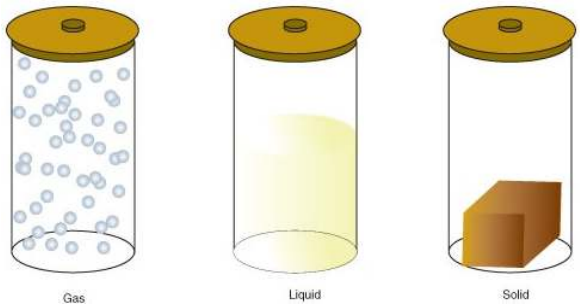


Figure **2.1.1**: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

What Determines a Substance's State?

Which state a substance is in depends partly on temperature and air pressure. For example, at the air pressure found at sea level, water exists as a liquid at temperatures between $0°C$ and $100°C$. Above $100°C$, water exists as a gas (water vapor). Below $0°C$, water exists as a solid (ice). Different substances have a different range of temperatures at which they exist in each state. For example, oxygen is a gas above $-183°C$, but iron is a gas only above $2861°C$. These differences explain why some substances are always solids at normal Earth temperatures, whereas others are always gases or liquids.

Water can take many forms. At low temperatures (below $0°C$), it is a solid. It is a liquid between $0°C$ and $100°C$. While at temperatures above $100°C$, water is a gas (steam). The state the water is in depends upon the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties.

Table **2.1.1**: Characteristics of each Phase of Matter

	Gas	Liquid	Solid
Shape	no definite shape (takes the shape of its container)	no definite shape (takes the shape of its container)	definite shape (rigid)
Volume	particles move in random motion with little or no attraction to each other	has definite volume	definite volume
Mobility	particles move in random motion with little or no attraction to each other	particles are free to move over each other, but are still attracted to each other	particles vib

	Gas	Liquid	Solid
			rate around fixed axes
Compressibility	highly compressible	weakly compressible	weakly compressible

> *Technically speaking a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.*

Changing States

Matter constantly goes through cycles that involve changing states (also called change phases). Water and all the elements important to organisms, including carbon and nitrogen, are constantly recycled on Earth. As matter moves through its cycles, it changes state repeatedly. For example, in the water cycle, water repeatedly changes from a gas to a liquid or solid and back to a gas again. How does this happen?

Adding energy to matter gives its atoms or molecules the ability to resist some of the forces holding them together. For example, heating ice to its **melting point** gives its molecules enough energy to move. The ice melts and becomes liquid water. Similarly, heating liquid water to its **boiling point** gives its molecules enough energy to pull apart from one another so they no longer have contact. The liquid water vaporizes and becomes water vapor.

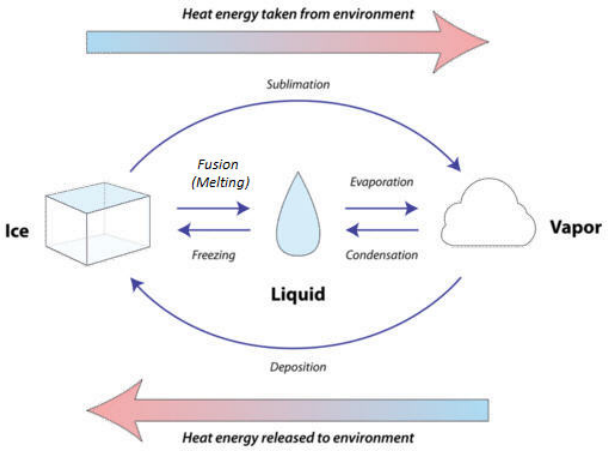


Figure **2.1.2**: Matter can move between any two states (or phases) of matter depending on the pressure and temperature conditions. Although the figure shows the states for water, these names apply to all substances. *Use of the word fusion for melting is based on its Latin roots.*

The temperature of the melting and boiling points depend on the identity of the substance and the atmospheric pressure. Each substance has its own boiling and melting points that depend on the properties of the substance, including the strength of its intermolecular forces. As an example, the values for water are given in Table **2.1.1**. Note how the boiling point of water varies greatly with pressure.

Table **2.1.1**: Boiling point of water as a function of pressure

Altitude (ft)	Pressure (atm)	Boiling Point (°C)
-500	1.05	100.5
0	1.00	100
4000	0.892	96
7000	0.797	93

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2.2: Kinetic-Molecular Theory

Learning Outcomes

- Define pressure and describe how gases exert pressure.
- Convert between units of gas pressure (**atm**, **mmHg**, **torr**, and **Pa**).
- Relate temperature to average kinetic energy.
- Relate mass to molecular speed.
- Describe the behavior of an ideal gas.

The **kinetic-molecular theory** *is a theory that explains the states of matter and is based on the idea that matter is composed of tiny particles that are always in motion*. The theory helps explain observable properties and behaviors of solids, liquids, and gases. However, the theory is most easily understood as it applies to gases. The theory applies specifically to a model of a gas called an ideal gas. An **ideal gas** *is an imaginary gas whose behavior perfectly fits all the assumptions of the kinetic-molecular theory*. In reality, gases are not ideal, but they are very close to being so under most everyday conditions.

The kinetic-molecular theory, as it applies to gases, has five basic assumptions.

1. **Gases consist of very large numbers of tiny spherical particles that are far apart from one another compared to their size**. The particles of a gas may be either atoms or molecules. The distance between the particles of a gas is much, much greater than the distances between the particles of a liquid or a solid. Most of the volume of a gas, therefore, is composed of the empty space between the particles. In fact, the volume of the particles themselves is considered to be insignificant compared to the volume of the empty space.
2. **Gas particles are in constant rapid motion in random directions**. The fast motion of gas particles gives them a relatively large amount of kinetic energy. Recall that kinetic energy is the energy that an object possesses because of its motion. The particles of a gas move in a straight line until they collide with another particle or with one of the walls of their container (see figure below).
3. **Collisions between gas particles and between particles and the container walls are elastic collisions**. An elastic collision is one in which there is no overall loss of kinetic energy. Kinetic energy may be transferred from one particle to another during an elastic collision, but there is no change in the total energy of the colliding particles.
4. **There are no forces of attraction or repulsion between gas particles**. Attractive forces are responsible for particles of a real gas condensing together to form a liquid. It is assumed that the particles of an ideal gas have no such attractive forces. The motion of each particle is completely independent of the motion of all other particles.
5. **The average kinetic energy of gas particles is dependent upon the temperature of the gas**. As the temperature of a gas is increased, its component particles begin to move faster, resulting in an increase in their kinetic energies. Not all particles in a given sample have the same speed, so the sample will contain particles with a range of different kinetic energies. However, the average kinetic energy of the particles in a sample is proportional to its temperature.

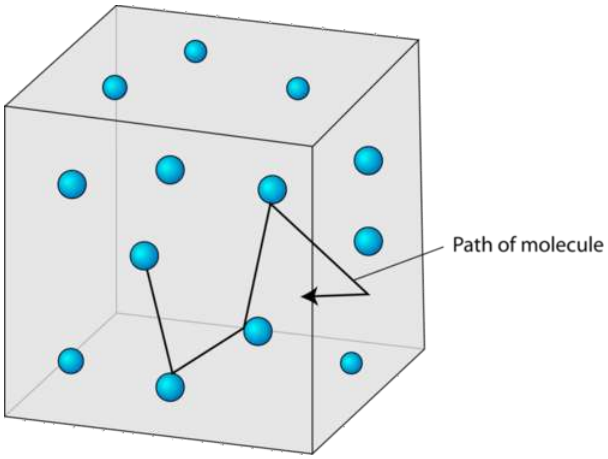


Figure **2.2.1**: Gas particles move in a random, linear fashion according to the kinetic-molecular theory. The space between particles is very large compared to the size of the particles.

Gas Pressure

Pressure *is defined as the force per unit area on a surface.*

$$\text{Pressure} = \frac{\text{force}}{\text{area}} \tag{2.2.1}$$

When a person stands on the floor, his feet exert pressure on the surface. That pressure is related to both the mass of the person and the surface area of his feet. If the person were holding a heavy object, the pressure would increase because of a greater force. Alternatively, if the person stands on his toes, the pressure also increases because of a decrease in the surface area.

Gas molecules also exert pressure. Earth's atmosphere exerts pressure because gravity acts on the huge number of gas particles contained in the atmosphere, holding it in place. Pressure is also exerted by small samples of gas, such as the outward pressure exerted by the gas inside a balloon. **Gas pressure** *is the pressure that results from collisions of gas particles with an object*. Inside the balloon, the gas particles collide with the balloon's inner walls. It is those collisions that keep the balloon inflated. If the gas particles were to suddenly stop moving, the balloon would instantly deflate. The figure below is an illustration of gas particles exerting pressure inside a container.

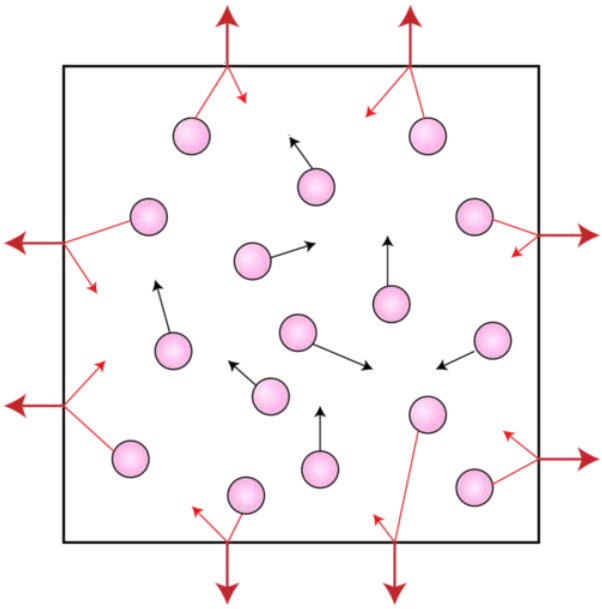


Figure **2.2.2**: Gas pressure results from collisions with the surface of its container.

Measuring Pressure

Atmospheric pressure *is the pressure exerted by the gas particles in Earth's atmosphere as those particles collide with objects*. A **barometer** *is an instrument used to measure atmospheric pressure*. A traditional mercury barometer consists of an evacuated tube immersed in a container of mercury. Air molecules from the atmosphere push down on the outer surface of the mercury, but, because the inside of the tube is a vacuum, there is no corresponding downward push on the mercury in the tube. As a result, the mercury rises inside the tube. The height to which the mercury rises is dependent on the external air pressure.

At sea level, a mercury column will rise a distance of $760\ \text{mm}$. This atmospheric pressure is reported as $760\ \text{mm Hg}$ (millimeters of mercury). At higher altitudes, the atmospheric pressure is lower, so the column of mercury will not rise as high. For example, on the summit of Mt. Everest (at an elevation of $8848\ \text{m}$), the air pressure is $253\ \text{mm Hg}$. Atmospheric pressure is also slightly dependent on weather conditions.

A more convenient barometer, called an aneroid barometer, measures pressure by the expansion and contraction of a small spring within an evacuated metal capsule.

Units of Gas Pressure

A barometers measures gas pressure by the height of the column of mercury. One unit of gas pressure is the millimeter of mercury (mm Hg). An equivalent unit to the mm Hg is called the torr, in honor of the inventor of the barometer, Evangelista Torricelli. The

pascal (**Pa**) *is the standard unit of pressure*. A pascal is a very small amount of pressure, so a more useful unit for everyday gas pressures is the kilopascal (**kPa**). A kilopascal is equal to 1000 pascals. Another commonly used unit of pressure is the atmosphere (**atm**). Standard atmospheric pressure is called **1 atm** of pressure and is equal to **760 mm Hg** and **101.3 kPa**. The relationships between the most common units of pressure are shown below.

$$1\ \text{atm} = 760\ \text{mm Hg} = 760\ \text{torr} = 101.3\ \text{kPa} \tag{2.2.2}$$

Example 2.2.1

The atmospheric pressure in a mountainous location is measured to be **613 mm Hg**. What is this pressure in **atm** and in **kPa**?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Given: **613 mm Hg**
- **1 atm = 760 mm Hg**
- **101.3 kPa = 760 mm Hg**

Unknown

- Pressure **=? atm**
- Pressure **=? kPa**

Use conversion factors from the equivalent pressure units to convert from **mm Hg** to **atm** and from **mm Hg** to **kPa**.

Step 2: Solve.

$$613\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}} = 0.807\ \text{atm}$$

$$613\ \text{mm Hg} \times \frac{101.3\ \text{kPa}}{760\ \text{mm Hg}} = 81.7\ \text{kPa}$$

Step 3: Think about your result.

The air pressure is about **80%** of the standard atmospheric pressure at sea level. The standard pressure of **760 mm Hg** can be considered to have three significant figures.

Kinetic Energy and Temperature

As stated in the kinetic-molecular theory, the temperature of a substance is related to the average kinetic energy of the particles of that substance. When a substance is heated, some of the absorbed energy is stored within the particles, while some of the energy increases the speeds at which the particles are moving. This is observed as an increase in the temperature of the substance.

Average Kinetic Energy

At any given temperature, not all of the particles in a sample of matter have the same kinetic energy. Instead, the particles display a wide range of kinetic energies. Most of the particles have a kinetic energy near the middle of the range. However, some of the particles have kinetic energies a great deal lower or a great deal higher than the average (see figure below).

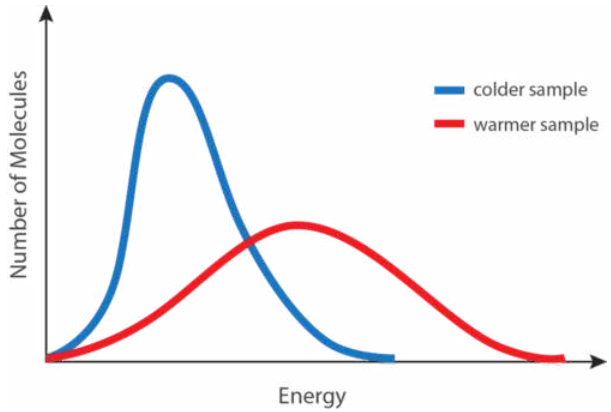


Figure **2.2.3**: A distribution of molecular kinetic energies as a function of temperature. The blue curve is for a low temperature, while the red curve is for a high temperature.

The blue curve shown (see figure above) is for a sample of matter at a relatively low temperature, while the red curve is for a sample at a relatively high temperature. In both cases, most of the particles have intermediate kinetic energies, close to the average. Notice that as temperature increases, the range of kinetic energies increases and the distribution curve "flattens out".

At a given temperature, the particles of any substance have the same average kinetic energy. At room temperature, the molecules in a sample of liquid water have the same average kinetic energy as the molecules in a sample of oxygen gas or the ions in a sample of sodium chloride.

Absolute Zero

As a sample of matter is continually cooled, the average kinetic energy of its particles decreases. Eventually, one would expect the particles to stop moving completely. **Absolute zero** *is the temperature at which the motion of particles theoretically ceases.* Absolute zero has never been attained in the laboratory, but temperatures on the order of $1 \times 10^{-10}\ \mathrm{K}$ have been achieved. The Kelvin temperature scale is based on this theoretical limit, so absolute zero is equal to $0\ \mathrm{K}$. The Kelvin temperature of a substance is directly proportional to the average kinetic energy of the particles of the substance. For example, the particles in a sample of hydrogen gas at $200\ \mathrm{K}$ have twice the average kinetic energy as the particles in a hydrogen sample at $100\ \mathrm{K}$.

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2.3: Gas Laws

Learning Objectives

- To predict the properties of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (P), volume (V), temperature (T, in kelvins), and amount of material expressed in moles (n). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}} \tag{2.3.1}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{2.3.2}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 2.3.2, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

Example 2.3.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

Exercise 2.3.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

Example 2.3.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are

looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56\text{ atm})(7.02\text{ L}) = (0.987\text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02\text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02\text{ L})}{0.987} = \mathbf{V_f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

Exercise 2.3.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 2.3.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

Solution

This example is similar to Example **2.3.2**, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56\text{ atm} \times \frac{760\text{ torr}}{1\text{ atm}} = 1,190\text{ torr}$$

Now we can use Boyle's law:

$$(1{,}190\text{ torr})(7.02\text{ L}) = (1{,}775\text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1{,}190)(7.02\text{ L}) = (1{,}775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\mathbf{V_f} = \frac{(1,190)(7.02\text{ L})}{1,775} = 4.71\text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 2.336\text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\mathbf{V_f} = \frac{(1.56\text{ atm})(7.02\text{ L})}{2.336\text{ atm}} = 4.69\text{ L}$.

Exercise 2.3.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is

$$V \propto T \tag{2.3.3}$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273$$

Thus, it is easy to convert from one temperature scale to another.

The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

Example 2.3.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

Exercise 2.3.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{2.3.4}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant.

Example 2.3.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Solution

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20°C + 273 = 293\ K = T_i \quad 60°C + 273 = 333\ K = T_f$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ L}{293\ K} = \frac{V_f}{333\ K}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333\ K)(20.0\ L)}{293\ K} = V_f$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 2.3.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to −35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Answer

3.91 L

Gay-Lussac's Law

Another simple gas law relates the pressure of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased in a container at constant volume, its pressure increases. The way to write this mathematically is

$$P \propto T \tag{2.3.5}$$

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f} \tag{2.3.6}$$

where P_i and T_i are the initial pressure and temperature, and P_f and T_f are the final pressure and temperature. The restriction on its use is that the volume of the gas and the amount of gas must remain constant. Just like in Charles'law, the temperature of a gas sample should always be expressed in a Kelvin temperature when applying Gay-Lussac's Law.

Combined Gas Law

The combined gas law brings Boyle's, Charles's land Gay-Lussac´s laws together to relate pressure, volume, and temperature changes of a gas sample:

Double subscripts: use braces to clarify

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

Example 2.3.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\ \text{atm})(10.5\ \text{L})}{300\ \text{K}} = \frac{(0.750\ \text{atm})(\text{V}_\text{f})}{350\ \text{K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\text{V}_\text{f} = \frac{(1.50\ \text{atm})(10.5\ \text{L})(350\ \text{K})}{(300\ \text{K})(0.750\ \text{atm})} = 24.5\ \text{L}$$

Note how all the units cancel except the unit for volume.

Exercise 2.3.6

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

Example 2.3.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°\text{C} + 273 = 295\ \text{K} = T_i$$

$$11°\text{C} + 273 = 284\ \text{K} = T_f$$

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = \text{P}_\text{i}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times \text{V}_\text{f}}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = \text{V}_\text{f}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

Exercise 2.3.7

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

Avogadro´s law

Avogadro's law relates the volume of a gas to the amount of gas present. The law says that, at constant temperature and pressure, the volume of a gas is directly proportional to the amount of moles (or grams) of a gas:

$$\text{V} \propto n \tag{2.3.7}$$

In this equation, V is volume and n is amount of moles. For comparing the same substance under two different sets of conditions, the law can be usefully expressed as follows:

$$\frac{\text{V}_\text{i}}{\text{n}_\text{i}} = \frac{\text{V}_\text{f}}{\text{n}_\text{f}} \tag{2.3.8}$$

where V_i and n_i are the initial volume and number of moles, and V_f and n_f are the final volume and number of moles.

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT \tag{2.3.9}$$

In this equation, P is pressure, V is volume, n is amount of moles, and T is temperature. R is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts i and f to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of R depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of R is as follows:

$$\text{R} = 0.08205\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \tag{2.3.10}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 2.3.8

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$(3.995\ \text{atm}) \times V = (1.45\ \text{mol}) \left(0.08205\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (298\ \text{K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)\ \text{L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

Exercise 2.3.8

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \text{atm}) \times V = (1.00\ \text{mol}) \left(0.08205\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273\ \text{K}) \tag{2.3.11}$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

$$1\ \text{mol gas} = 22.4\ \text{L (at STP)}$$

Example 2.3.9

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \text{L}\ C_3H_6 \times \frac{1\ \text{mol}}{22.4\ \text{L}} = 4.46\ \text{mol}\ C_3H_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

Exercise 2.3.9

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags (Figure **2.3.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,NaN_3(s) \rightarrow 3\,N_2(g) + 2\,Na(s) \tag{2.3.12}$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure **2.3.3**: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 \ldots = \sum_i P_i \tag{2.3.13}$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i \tag{2.3.14}$$

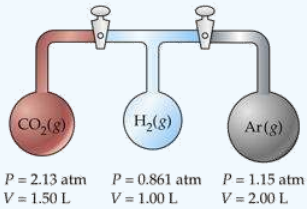
There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

Example 2.3.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?
b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.



Solution

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO_2 only, denoted by subscripts a.

For CO_2,

$$P_aV_a = (2.13\ atm)(1.50\ L) = 3.19\ L \cdot atm \tag{2.3.15}$$

Adding the PV products for each separate container, we obtain

$$\sum_i P_iV_i = 6.36\ L \cdot atm = n_TRT \tag{2.3.16}$$

We will call this sum P_1V_1. After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2.

From Boyle's law (2.3.2),

$$P_1V_1 = P_2V_2 = 6.36\ L \cdot atm \tag{2.3.17}$$

$$V_2 = \sum_i V_i = 4.50\ L \tag{2.3.18}$$

Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part *(b)*, note that the number of moles of each gas is $n = PV/RT$. The mole fraction of any one gas is $X_i = n_i/n_T$. For CO_2, this works out to (3.19/RT) / (6.36/RT) = 0.501. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n \tag{2.3.19}$$

or

$$P_n = \frac{n}{P_{Total}} \tag{2.3.20}$$

Table **2.3.1**: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2} = 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

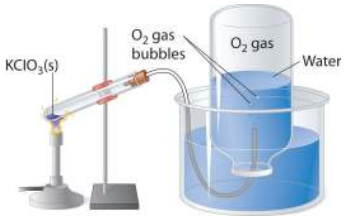


Figure **2.3.1**:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 2.3.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latm mol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

Henry's Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in

equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{gas} \tag{2.3.21}$$

where

Henry's Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry's law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2\,(g)}$ at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Application of Henry's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

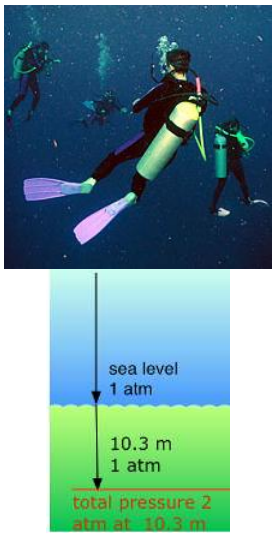


Figure **2.3.2**: Scuba Dviging actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate's degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor's offices, nursing homes, or patient's homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

Concept Review Exercises

1. What properties do the gas laws help us predict?
2. What makes the ideal gas law different from the other gas laws?

Answers

1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
2. The ideal gas law does not require that the properties of a gas change.

Key Takeaway

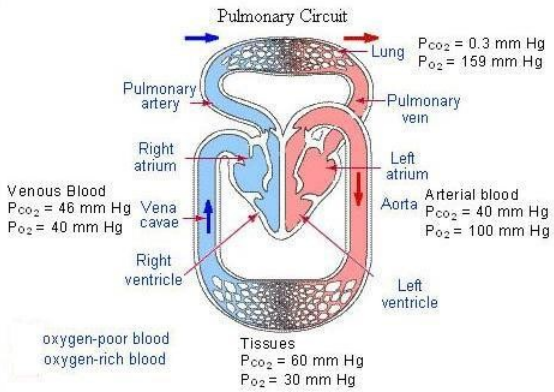
- The physical properties of gases are predictable using mathematical formulas known as gas laws.
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

Exercises

1. What conditions of a gas sample should remain constant for Boyle's law to be used?
2. What conditions of a gas sample should remain constant for Charles's law to be used?
3. Does the identity of a gas matter when using Boyle's law? Why or why not?
4. Does the identity of a gas matter when using Charles's law? Why or why not?
5. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
6. A sample of helium gas in a piston has a volume of 86.4 mL under a pressure of 447 torr. What will be the volume of the helium if the pressure on the piston is increased to 1,240 torr? Assume that the temperature and the amount of the gas remain constant.
7. If a gas has an initial pressure of 24,650 Pa and an initial volume of 376 mL, what is the final volume if the pressure of the gas is changed to 775 torr? Assume that the amount and the temperature of the gas remain constant.
8. A gas sample has an initial volume of 0.9550 L and an initial pressure of 564.5 torr. What would the final pressure of the gas be if the volume is changed to 587.0 mL? Assume that the amount and the temperature of the gas remain constant.
9. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is 18°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and amount of the gas remain constant.
10. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is −10°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and the amount of the gas remain constant.
11. An air/gas vapor mix in an automobile cylinder has an initial temperature of 450 K and a volume of 12.7 cm^3. The gas mix is heated to 565°C. If pressure and amount are held constant, what is the final volume of the gas in cubic centimeters?
12. Given the following conditions for a gas: V_i = 0.665 L, T_i = 23.6°C, V_f = 1.034 L. What is T_f in degrees Celsius and kelvins?
13. Assuming the amount remains the same, what must be the final volume of a gas that has an initial volume of 387 mL, an initial pressure of 456 torr, an initial temperature of 65.0°C, a final pressure of 1.00 atm, and a final temperature of 300 K?

14. When the nozzle of a spray can is depressed, 0.15 mL of gas expands to 0.44 mL, and its pressure drops from 788 torr to 1.00 atm. If the initial temperature of the gas is 22.0°C, what is the final temperature of the gas?
15. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.
16. Use a standard conversion factor to determine a value of the ideal gas law constant *R* that has units of L•torr/mol•K.
17. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
18. How many moles of gas are there in a 0.066 L sample at 298 K and a pressure of 0.154 atm?
19. A 0.334 mol sample of carbon dioxide gas is confined to a volume of 20.0 L and has a pressure of 0.555 atm. What is the temperature of the carbon dioxide in kelvins and degrees Celsius?
20. What must *V* be for a gas sample if *n* = 4.55 mol, *P* = 7.32 atm, and *T* = 285 K?
21. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?
22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of −86.0°C?
23. A mixture of the gases N_2, O_2, and Ar has a total pressure of 760 mm Hg. If the partial pressure of N_2 is 220 mm Hg and of O_2 is 470 mm Hg, What is the partial pressure of Ar?
24. What percent of the gas above is Ar?
25. Apply Henry's Law to the diagram below to explain:

why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



Answers

1. temperature and amount of the gas
2. pressure and amount of the gas
3. The identity does not matter because the variables of Boyle's law do not identify the gas.
4. The identity does not matter because the variables of Charles law do not identify the gas.
5. 3.79 L
6. 31.1 mL
7. 92.1 mL

8. 918.4 torr

9. 1.07 L

10. 1.18 L

11. 23.7 cm^3

12. 461 K; 188^0C

13. 206 mL

14. 835 K; 562^0C

15. The ideal gas law confirms that 22.4 L equals 1 mol.

16. $\frac{760\ torr}{1\ atm}$

17. 1.63 mol

18. 4.2 x 10^{-4} mol

19. 405 K; 132°C

20. 14.5 L

21. 0.151 atm

22. 18.2 atm

23. 70 mm Hg

24. 9.2%

25. Gases diffuse from high concentration to low concentration (Henry's Law). The partial pressure of **oxygen** is high in the **alveoli** and low in the **blood** of the pulmonary capillaries. As a result, **oxygen diffuses** across the respiratory membrane from the **alveoli** into the **blood**. It's also higher partial pressure in the blood than in the tissues, hence it transfers to the tissues. On the other hand, carbon dioxide **diffuses** from the tissues (highest CO_2 partial pressure) and across the respiratory membrane from the **blood** into the **alveoli** and out **to the atmosphere.**

Attribution and citations

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2.4: Diffusion and Effusion- Graham's Law

We usually cannot see gases, so we need methods to detect their movements indirectly. The relative rates of diffusion of ammonia to hydrogen chloride can be observed in a simple experiment. Cotton balls are soaked with solutions of ammonia and hydrogen chloride (hydrochloric acid) and attached to two different rubber stoppers. These are simultaneously plugged into either end of a long glass tube. The vapors of each travel down the tube at different rates. Where the vapors meet, they react to form ammonium chloride ($\mathbf{NH_4Cl}$), a white solid that appears in the glass tube as a ring.

Graham's Law

When a person opens a bottle of perfume in one corner of a large room, it doesn't take very long for the scent to spread throughout the entire room. Molecules of the perfume evaporate and the vapor spreads out to fill the entire space. **Diffusion** is the tendency of molecules to move from an area of high concentration to an area of low concentration until the concentration is uniform. While gases diffuse rather quickly, liquids diffuse much more slowly. Solids essentially do not diffuse.

A related process to diffusion is effusion. **Effusion** is the process of a confined gas escaping through a tiny hole in its container. Effusion can be observed by the fact that a helium-filled balloon will stop floating and sink to the floor after a day or so. This is because the helium gas effuses through tiny pores in the balloon. Both diffusion and effusion are related to the speed at which various gas molecules move. Gases that have a lower molar mass effuse and diffuse at a faster rate than gases that have a higher molar mass.

Scottish chemist Thomas Graham (1805-1869) studied the rates of effusion and diffusion of gases. **Graham's law** states that the rate of effusion or diffusion of a gas is inversely proportional to the square root of the molar mass of the gas. Graham's law can be understood by comparing two gases (**A** and **B**) at the same temperature, meaning the gases have the same kinetic energy. The kinetic energy of a moving object is given by the equation $KE = \frac{1}{2}mv^2$ where m is mass and v is velocity. Setting the kinetic energies of the two gases equal to one another gives:

$$\frac{1}{2}m_Av_A^2 = \frac{1}{2}m_Bv_B^2$$

The equation can be rearranged to solve for the ratio of the velocity of gas **A** to the velocity of gas **B** $\left(\frac{v_A}{v_B}\right)$.

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \quad \text{which becomes} \quad \frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$$

For the purposes of comparing the rates of effusion or diffusion of two gases at the same temperature, the molar masses of each gas can be used in the equation for m.

Example **2.4.1**

Calculate the ratio of diffusion rates of ammonia gas ($\mathbf{NH_3}$) to hydrogen chloride ($\mathbf{HCl}$) at the same temperature and pressure.

Solution:

Step 1: List the known quantities and plan the problem.

Known

- Molar mass $\mathbf{NH_3} = 17.04\ \mathbf{g/mol}$
- Molar mass $\mathbf{HCl} = 36.46\ \mathbf{g/mol}$

Unknown

Substitute the molar masses of the gases into Graham's law and solve for the ratio.

Step 2: Solve.

$$\frac{v_{NH_3}}{v_{HCl}} = \sqrt{\frac{36.46\ \mathbf{g/mol}}{17.04\ \mathbf{g/mol}}} = 1.46$$

The rate of diffusion of ammonia is 1.46 times faster than the rate of diffusion of hydrogen chloride.

Step 3: Think about your result.

Since ammonia has a smaller molar mass than hydrogen chloride, the velocity of its molecules is greater and the velocity ratio is larger than 1.

Summary

- Diffusion is the tendency of molecules to move from an area of high concentration to an area of low concentration until the concentration is uniform.
- Effusion is the process of a confined gas escaping through a tiny hole in its container.
- Graham's law states that the rate of effusion or diffusion of a gas is inversely proportional to the square root of the molar mass of the gas.

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2.5: Changes in State and Heating Curves

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure **2.5.1**.

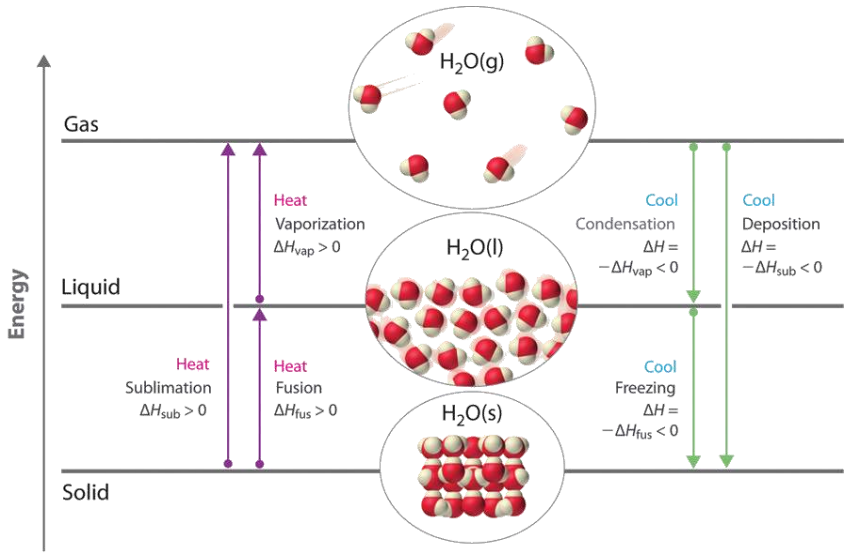


Figure **2.5.1**: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure **2.5.1**.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table **2.5.1**.

Table **2.5.1**: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*



Figure **2.5.2**: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure **2.5.2**); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure **2.5.1**, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{2.5.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we

exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure **2.5.1**—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure **2.5.3** shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

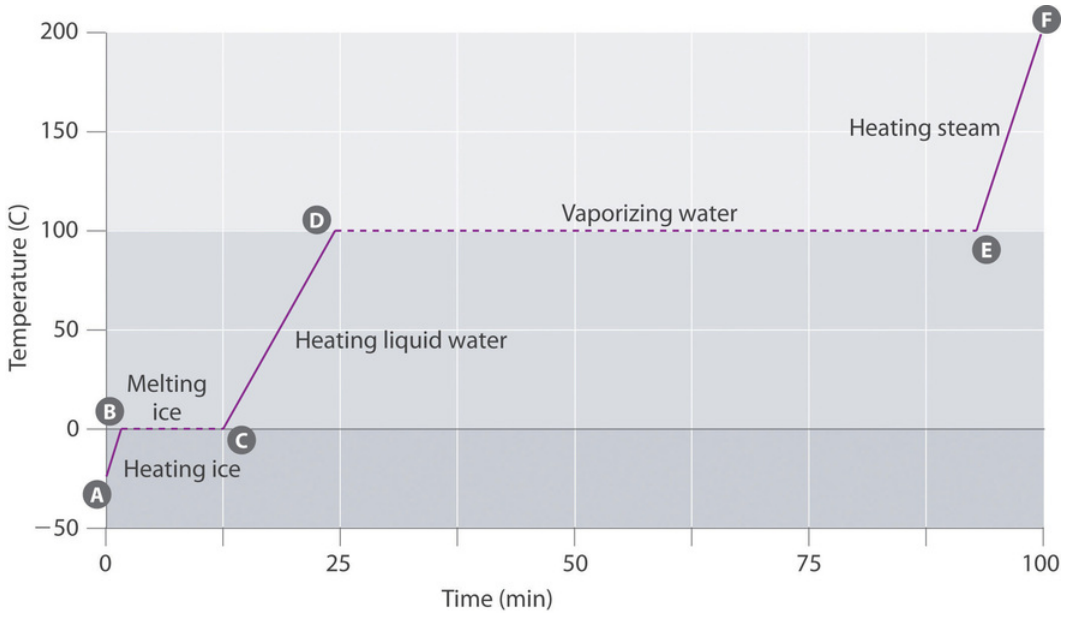


Figure **2.5.3**: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up

higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure **2.5.3**, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure **2.5.3**, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes "bumping" when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **2.5.4** plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure **2.5.3**, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

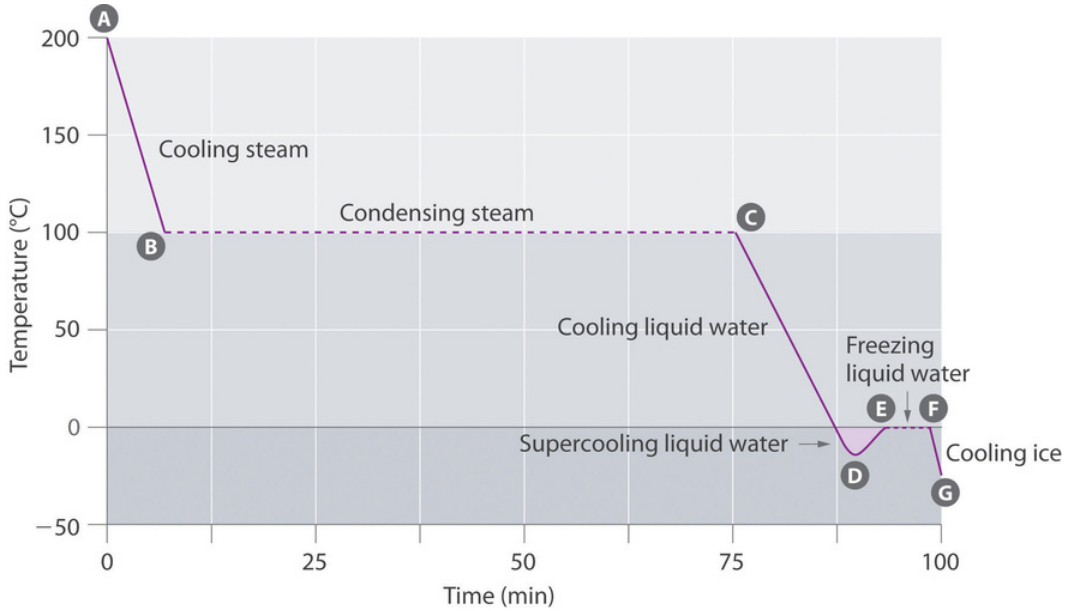


Figure **2.5.4**: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.



A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 2.5.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1\,mol}{18.02\,g} \cdot 6.01\,kJ/mol \\ &= 16.7\,kJ \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$\begin{aligned} q_{tea} &= -16,700J = 500mL \cdot \frac{1.00\,g}{1\,mL} \cdot 4.184J/(g \bullet °C)\Delta T \\ \Delta T &= -7.98°C = T_f - T_i \\ &= 12.02°C \end{aligned}$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 0.0°C) \\ &= 209.2J/°C \cdot T_f \end{aligned}$$

$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 12.02°C) = 2092J/°C \cdot T_f - 25,150J$$

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J$$

$$2301.2J/°C \cdot T_f = 25,150J$$

$$T_f = 10.9°C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 2.5.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example **2.5.1**

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*.

Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

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CHAPTER OVERVIEW

3: Solutions and Colloids

3.1: Some Basic Definitions
3.2: Solubility
3.3: The Dissolving Process
3.4: Concentrations of Solutions
3.5: Stoichiometry calculations with solutions
3.6: Colligative Properties of Solutions
3.7: Colligative Properties of Ionic Solutes
3.8: Colloids and Suspensions
3.9: Dialysis

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3.1: Some Basic Definitions

Learning Objective

- Learn some terminology involving solutions.
- Recognize which terminology is qualitative and which terminology is quantitative.
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. "Major" and "minor" indicate which component has the greater or lesser presence by mass or moles, respectively. Sometimes this becomes confusing, especially when considering substances with very different molar masses. We will confine the discussion here to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 3.1.1: Sugar Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is sucrose, so it is the solute. Water—the majority component—is the solvent. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 3.1.1

A solution is made by dissolving 3.33 g of HCl(g) in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH_3OH

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. What is it that makes a solute soluble in some solvents but not others?

The answer is **intermolecular interactions.** The intermolecular interactions include London dispersion forces, dipole-dipole interactions, hydrogen bonding, and ion-dipole. From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general rule that **"like dissolves like"** for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

Example 3.1.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Exercise 3.1.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.
- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

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3.2: Solubility

Learning Outcomes

- List examples of solutions made from different solute-solvent combinations.
- Distinguish between saturated and unsaturated solutions.
- Explain the effects of temperature on the solubility of solids and gases.
- Use a solubility curve to determine the solubilities of substances at various temperatures.
- Explain the effect of pressure on the solubility of gases.

Previously, we looked at the primary characteristics of a solution and how water is able to dissolve solid solutes. There are many examples of solutions that do not involve water at all, or solutions that involve solutes that are not solids. The table below summarizes the possible combinations of solute-solvent states, along with examples of each.

Table **3.2.1**: Solute-Solvent Combinations

Solute State	Solvent State	Example
liquid	gas	water in air
gas	gas	oxygen in nitrogen (gas mixture)
solid	liquid	salt in water
liquid	liquid	alcohol in water
gas	liquid	carbon dioxide in water
solid	solid	zinc in copper (brass alloy)
liquid	solid	mercury in silver and tin (dental amalgam)

Air is a homogeneous mixture of many different gases and, therefore, qualifies as a solution. Solid-solid solutions, such as brass, bronze, and sterling silver, are called alloys. Fish depend on oxygen gas that is dissolved in the water found in oceans, lakes and rivers (see figure below). While solid-liquid and aqueous solutions comprise the majority of solutions encountered in the chemistry laboratory, it is important to be aware of the other possibilities.



Figure **3.2.1**: Large aquariums like this salt-water tank have air continually bubbled into the water so that the fish have enough dissolved oxygen to breathe.

Rate of Dissolving

We know that the dissolving of a solid by water depends upon the collisions that occur between the solvent molecules and the particles in the solid crystal. Anything that can be done to increase the frequency of those collisions and/or to give those collisions more energy will increase the rate of dissolving. Imagine that you were trying to dissolve some sugar in a glassful of tea. A packet

of granulated sugar would dissolve faster than a cube of sugar. The rate of dissolving would be increased by stirring, or agitating the solution. Finally, the sugar would dissolve faster in hot tea than it would in cold tea.

Surface Area

The rate at which a solute dissolves depends upon the size of the solute particles. Dissolving is a surface phenomenon, since it depends on solvent molecules colliding with the outer surface of the solute. A given quantity of solute dissolves faster when it is ground into small particles than if it is in the form of a large chunk, because more surface area is exposed. The packet of granulated sugar exposes far more surface area to the solvent and dissolves more quickly than the sugar cube.

Agitation of the Solution

Dissolving sugar in water will occur more quickly if the water is stirred. The stirring allows fresh solvent molecules to continually be in contact with the solute. If it is not stirred, then the water right at the surface of the solute becomes saturated with dissolved sugar molecules, meaning that it is more difficult for additional solute to dissolve. The sugar cube would eventually dissolve because random motions of the water molecules would bring enough fresh solvent into contact with the sugar, but the process would take much longer. It is important to realize that neither stirring nor breaking up a solute affect the overall amount of solute that dissolves. It only affects the rate of dissolving.

Temperature

Heating up the solvent gives the molecules more kinetic energy. The more rapid motion means that the solid or liquid solvent molecules collide with the solute with greater frequency, and the collisions occur with more force. Both factors increase the rate at which the solid or liquid solute dissolves. As we will see in the next section, a temperature change not only affects the rate of dissolving, but it also affects the amount of solute that can be dissolved.

Types of Solutions

Table salt (NaCl) readily dissolves in water. Suppose that you have a beaker of water to which you add some salt, stirring until it dissolves. Then you add more, and that dissolves as well. If you keep adding more and more salt, eventually you will reach a point at which no more of the salt will dissolve, no matter how long or how vigorously you stir it. Why? On the molecular level, we know that the action of the water causes the individual ions to break apart from the salt crystal and enter the solution, where they remain hydrated by water molecules. What also happens is that some of the dissolved ions collide back again with the crystal and remain there. **Recrystallization** *is the process of dissolved solute returning to the solid state*. At some point, the rate at which the solid salt is dissolving becomes equal to the rate at which the dissolved solute is recrystallizing. When that point is reached, the total amount of dissolved salt remains unchanged.

When the solution equilibrium point is reached and no more solute will dissolve, the solution is said to be saturated. A **saturated solution** *is a solution that contains the maximum amount of solute that is capable of being dissolved*. At $20°\mathrm{C}$, the maximum amount of NaCl that will dissolve in $100.\ \mathrm{g}$ of water is $36.0\ \mathrm{g}$. If any more NaCl is added past that point, it will not dissolve because the solution is saturated. What if more water is added to the solution instead? Now, more NaCl would be capable of dissolving, since there is additional solvent present. An **unsaturated solution** *is a solution that contains less than the maximum amount of solute that is capable of being dissolved*. The figure below illustrates the above process, and shows the distinction between unsaturated and saturated.

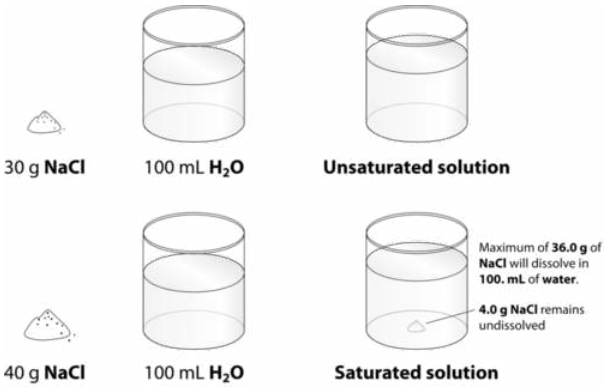


Figure 3.2.2: When 30.0 g of NaCl is added to 100 mL of water at 20°C, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has extra undissolved solute at the bottom of the container, must be saturated (see figure below).



Figure 3.2.3: A saturated solution of salt (sodium chloride) with undissolved solute remaining at the bottom of the measuring cup.

Solubility Values

The **solubility** *of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature*. Solubility is often measured in grams of solute per 100 g of solvent. The solubility of sodium chloride in water is 36.0 g per 100 g of water at 20°C. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. In other words, the solubility of sodium chloride would be different in another solvent. For the purposes of this text, the solubility of a substance will refer to aqueous solubility unless otherwise specified. Solubilities for different solutes have a very wide variation, as can be seen by the data presented in the table below.

Table 3.2.2: Solubility of Solutes at Different Temperatures (g solute in 100 g H_2O)

Substance	0°C	20°C	40°C	60°C	80°C	100°C
$AgNO_3$	122	216	311	440	585	733
$Ba(OH)_2$	1.67	3.89	8.22	20.94	101.4	__
$C_{12}H_{22}O_{11}$	179	204	238	287	362	487
$Ca(OH)_2$	0.189	0.173	0.141	0.121	__	0.07
KCl	28.0	34.2	40.1	45.8	51.3	56.3
KI	128	144	162	176	192	206
KNO_3	13.9	31.6	61.3	106	167	245
LiCl	69.2	83.5	89.8	98.4	112	128
NaCl	35.7	35.9	36.4	37.1	38.0	39.2
$NaNO_3$	73	87.6	102	122	148	180
CO_2 (1 atm)	0.335	0.169	0.0973	0.058	__	__
O_2 (1 atm)	0.00694	0.00537	0.00308	0.00227	0.00138	0.00

Factors Affecting Solubility

The solubility of a solid or a liquid solute in a solvent is affected by the temperature, while the solubility of a gaseous solute is affected by both the temperature and the pressure of the gas. We will examine the effects of temperature and pressure separately.

Temperature

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a solubility curve, which is a graph of the solubility vs. temperature. Examine the solubility curves shown (see figure below).

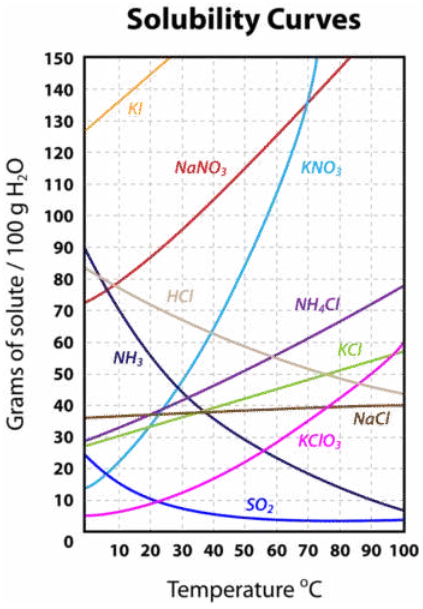


Figure **3.2.4**: A solubility curve is a graph of the solubility of a substance as a function of temperature.

Notice how the temperature dependence of **NaCl** is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of **NaCl**. The curve for KNO_3, on the other hand, is very steep; an increase in temperature dramatically increases the solubility of KNO_3.

Several substances listed on the graph - HCl, NH_3, and SO_2 - have solubilities that decrease as the temperature increases. These substances are all gases over the indicated temperature range when at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increases. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return back to the gas phase. As a result, the solubility of a gas decreases as the temperature increases. This has some profound environmental consequences. Industrial plants situated near bodies of water often use that water as a coolant, returning the warmer water back to the lake or river. This increases the overall temperature of the water, which lowers the quantity of dissolved oxygen, affecting the survival of fish and other organisms.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that $80\ g$ of KNO_3 is added to $100\ g$ of water at $30°C$. According to the solubility curve, approximately $48\ g$ of KNO_3 will dissolve at $30°C$. This means that the solution will be saturated, since $48\ g$ is less than $80\ g$. We can also determine that there will be $80 - 48 = 32\ g$ of undissolved KNO_3 remaining at the bottom of the container. Now, suppose that this saturated solution is heated to $60°C$. According to the curve, the solubility of KNO_3 at $60°C$ is about $107\ g$ the solution is now unsaturated, since it still contains only the original $80\ g$ of solute, all of which is now dissolved. Then, suppose the solution is cooled all the way down to $0°C$. The solubility at $0°C$ is about $14\ g$, meaning that $80 - 14 = 66\ g$ of the KNO_3 will recrystallize.

Some solutes, such as sodium acetate, do not recrystallize easily. Suppose an exactly saturated solution of sodium acetate is prepared at $50°C$. As it cools back to room temperature, crystals do not immediately appear in the solution, even though the solubility of sodium acetate is lower at room temperature. A **supersaturated solution** *is a solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature*. The recrystallization of the excess dissolved solute is a supersaturated solution can be initiated by the addition of a tiny crystal of solute, called a seed crystal. The seed crystal provides a nucleation site on which the excess dissolved crystals can begin to grow. Recrystallization from a supersaturated solution is typically very fast.

Pressure

Pressure has very little effect on the solubility of solids or liquids, but it has a significant effect on the solubility of gases. Gas solubility increases as the partial pressure of a gas above the liquid increases. Suppose a certain volume of water is in a closed container with the space above it occupied by carbon dioxide gas at standard pressure. Some of the CO_2 molecules come into contact with the surface of the water and dissolve into the liquid. Now suppose that more CO_2 is added to the space above the container, causing a pressure increase. More CO_2 molecules are now in contact with the water, so more of them dissolve. Thus the solubility increases as the pressure increases. As with a solid, the CO_2 that is undissolved reaches an equilibrium with the dissolved CO_2, represented by the following equation.

$$CO_2\,(g) \rightleftharpoons CO_2\,(aq) \tag{3.2.1}$$

At equilibrium, the rate of gaseous CO_2 dissolving is equal to the rate of dissolved CO_2 coming out of the solution.

When carbonated beverages are packaged, they are done so under high CO_2 pressure so that a large amount of carbon dioxide dissolves in the liquid. When the bottle is opened, equilibrium is disrupted because the CO_2 pressure above the liquid decreases. Immediately, bubbles of CO_2 rapidly exit the solution and escape out of the top of the open bottle. The amount of dissolved CO_2 decreases. If the bottle is left open for an extended period of time, the beverage becomes "flat" as more and more CO_2 comes out of the liquid.

The relationship of gas solubility to pressure is described by Henry's law, named after English chemist William Henry (1774 - 1836). **Henry's law** *states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.*

Supplemental Resources

- Solubility of Things: http://www.solubilityofthings.com/
- Solubility Curves: http://www.kentchemistry.com/links/K...lityCurves.htm
- Henry's Law: http://www.kentchemistry.com/links/K.../HenrysLaw.htm

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3.3: The Dissolving Process

Learning Outcomes

- Define a solution and describe the parts of a solution.
- Describe how an aqueous solution is formed from both ionic compounds and molecular compounds.
- Recognize that some compounds are insoluble in water.
- Describe the differences among strong electrolytes, weak electrolytes, and nonelectrolytes.

Forming a Solution

When one substance dissolves into another, a solution is formed. A **solution** *is a homogenous mixture consisting of a solute dissolved into a solvent.* The **solute** *is the substance that is being dissolved*, while the **solvent** *is the dissolving medium*. Solutions can be formed with many different types and forms of solutes and solvents. In this chapter, we will focus on solution where the solvent is water. An **aqueous solution** *is water that contains one or more dissolved substance.* The dissolved substances in an aqueous solution may be solids, gases, or other liquids.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time, and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will remain with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.



Figure 3.3.1: When a colored solution is passed through a filter, the entire solution, both solute and solvent, pass through unchanged.

The Dissolving Process

Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water. We will first examine the process that occurs when an ionic compound, such as table salt (sodium chloride), dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar; it has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see figure below).

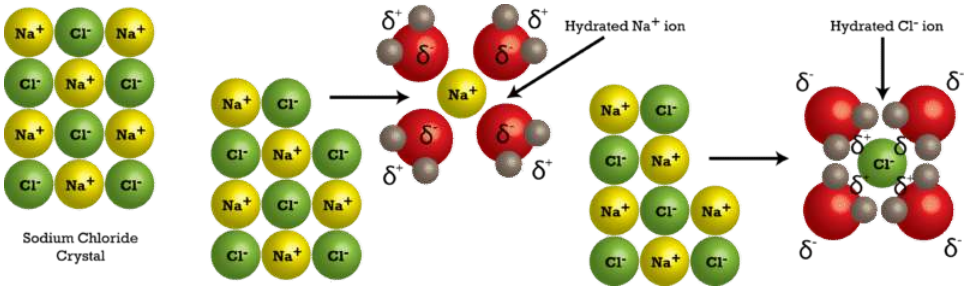


Figure 3.3.2: The process of an ionic sodium chloride crystal being dissolved and hydrated by water.

After coming apart from the crystal, *the individual ions are then surrounded by solvent particles in a process called* **solvation**. Note in the figure above that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** *is the process of solute particles being surrounded by water molecules arranged in a specific manner*. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is made of the molecular compound sucrose ($C_{12}H_{22}O_{11}$). Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but it *does not break the covalent bonds* between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated. The hydration shell around a molecule of sucrose is arranged so that its partially negative oxygen atoms are near the partially positive hydrogen atoms in the solvent, and vice versa.

Insoluble Compounds

Not all compounds dissolve well in water. Some ionic compounds, such as calcium carbonate ($CaCO_3$) and silver chloride ($AgCl$), are nearly insoluble. This is because the attractions between the ions in the crystal lattice are stronger than the attraction that the water molecules have for the ions. As a result, the crystal remains intact. The solubility of ionic compounds can be predicted using the solubility rules as shown in Table **3.3.1**.

Table* 3.3.1*: *Solubility rules for ionic compounds in water.*

Soluble compounds contain	Except when paired with
Group I metal cations or NH_4^+	None
CH_3COO^-, NO_3^-, ClO_3^-, or ClO_4^-	None
Cl^-, Br^-, or I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
SO_4^{2-}	Ag^+, Hg_2^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
Insoluble compounds contain	**Except when paired with**
CO_3^{2-}, CrO_4^{2-}, PO_4^{3-}, or SO_3^{2-}	Group I cations or NH_4^+
S^{2-} or OH^-	Group I cations or NH_4^+, or Ba^{2+}
Ag^+, Hg_2^{2+}, and Pb^{2+}	CH_3COO^-, NO_3^-, ClO_3^-, or ClO_4^-

Nonpolar compounds also do not dissolve in water. The attractive forces that operate between the particles in a nonpolar compound are weak dispersion forces. In order for a nonpolar molecule to dissolve in water, it would need to break up some of the hydrogen bonds between adjacent water molecules. In the case of an ionic substance, these favorable interactions are replaced by other attractive interactions between the ions and the partial charges on water. However, interactions between nonpolar molecules and water are less favorable than the interactions that water makes with itself. When a nonpolar liquid such as oil is mixed with water, two separate layers form, because the liquids will not dissolve into each other (see figure below). When a polar liquid like ethanol is mixed with water, they completely blend and dissolve into one another. *Liquids that dissolve in one another in all proportions are said to be* **miscible**. *Liquids that do not dissolve in one another are called* **immiscible**. The general rule for deciding if one substance is capable of dissolving another is "like dissolves like", where the property being compared is the overall polarity of the substance. For example, a nonpolar solid such as iodine will dissolve in nonpolar lighter fluid, but it will not dissolve in polar water.



Figure **3.3.3**: Water and oil form separate layers when they are mixed because the nonpolar oil will not dissolve into the polar water. The oil forms the top layer because it is less dense than water.

Electrolytes and Nonelectrolytes

An **electrolyte** *is a compound that conducts an electric current when it is dissolved in water or melted.* In order to conduct a current, a substance must contain mobile ions that can move from one electrode to the other. All ionic compounds are electrolytes. When ionic compounds dissolve, they break apart into ions, which are then able to conduct a current. Even insoluble ionic compounds, such as $\mathrm{CaCO_3}$, are considered electrolytes because they can conduct a current in the molten (melted) state.

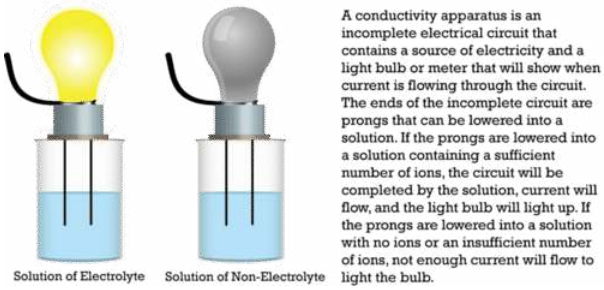


Figure **3.3.4**: An apparatus for testing the conductivity of a solution.

A **nonelectrolyte** *is a compound that does not conduct an electric current in either aqueous solution or in the molten state.* Many molecular compounds, such a sugar or ethanol, are nonelectrolytes. When these compounds dissolve in water, they do not produce ions. Illustrated below is the difference between an electrolyte and a nonelectrolyte.

Dissociation

Earlier, you saw how an ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** *is the separation of ions that occurs when a solid ionic compound dissolves*. Simply undo the crisscross method that you learned when writing chemical formulas for ionic compounds, and you are left with the components of an ionic dissociation equation. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equations. Shown below are dissociation equations for NaCl, $\mathrm{Ca(NO_3)_2}$, and $\mathrm{(NH_4)_3PO_4}$.

$$\mathrm{NaCl}\,(s) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) \tag{3.3.1}$$
$$\mathrm{Ca(NO_3)_2}\,(s) \rightarrow \mathrm{Ca^{2+}}\,(aq) + 2\mathrm{NO_3^-}\,(aq) \tag{3.3.2}$$
$$\mathrm{(NH_4)_3PO_4}\,(s) \rightarrow 3\mathrm{NH_4^+}\,(aq) + \mathrm{PO_4^{3-}}\,(aq) \tag{3.3.3}$$

One formula unit of sodium chloride dissociates into one sodium ion and one chloride ion. The calcium nitrate formula unit dissociates into one calcium ion and two nitrate ions, because the $2+$ charge of each calcium ion requires two nitrate ions (each with a charge of $1-$) to form an electrically neutral compound. The ammonium phosphate formula unit dissociates into three ammonium ions and one phosphate ion.

Do not confuse the subscripts of the atoms within the polyatomic ion for the subscripts that result from the crisscrossing of the charges that make the original compound neutral. The 3 subscript of the ntirate ion and the 4 subscript of the ammonium ion are part of the polyatomic ion and remain a part of the ionic formula after the compound dissociates. Notice that the compounds are solids (s) that become ions when dissolved in water, producing an aqueous solution (aq).



Figure **3.3.5**: Calcium nitrate is a typical ionic compound. In an aqueous solution, it dissociates into calcium ions and nitrate ions.

Nonelectrolytes do not dissociate when forming an aqueous solution. An equation can still be written that simply shows the solid going into solution. For example, the process of dissolving sucrose in water can be written as follows:

$$C_{12}H_{22}O_{11}\,(s) \rightarrow C_{12}H_{22}O_{11}\,(aq) \tag{3.3.4}$$

Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when the are in their pure state but become electrolytes when they are dissolved in water. Hydrogen chloride (HCl) is a gas in its pure molecular state and is a nonelectrolyte. However, when HCl is dissolved in water, it conducts a current well because the HCl molecule ionizes into hydrogen and chloride ions.

$$HCl\,(g) \rightarrow H^+\,(aq) + Cl^-\,(aq) \tag{3.3.5}$$

When HCl is dissolved into water, it is called hydrochloric acid. Ionic compounds and some polar compounds are completely broken apart into ions and thus conduct a current very well. A **strong electrolyte** *is a solution in which almost all of the dissolved solute exists as ions*.

Some other polar molecular compounds become electrolytes upon being dissolved into water but do not ionize to a very great extent. For example, nitrous acid (HNO_2) only partially ionizes into hydrogen ions and nitrite ions when dissolved in water. Aqueous nitrous acid is composed of only about 5% ions and 95% intact nitrous acid molecules A **weak electrolyte** *is a solution in which only a small fraction of the dissolved solute exists as ions*. The equation showing the ionization of a weak electrolyte utilizes an equilibrium arrow, indicating an equilibrium between the reactants and products.

$$HNO_2\,(aq) \rightleftharpoons H^+\,(aq) + NO_2{}^-\,(aq) \tag{3.3.6}$$

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3.4: Concentrations of Solutions

Learning Outcomes

- Define concentration.
- Use the terms concentrated and dilute to describe the relative concentration of a solution.
- Calculate the molarity of a solution.
- Calculate percentage concentration (m/m, v/v, m/v).
- Describe a solution whose concentration is in **ppm** or **ppb**.
- Use concentration units in calculations.
- Determine equivalents for an ion.
- Complete calculations relating equivalents to moles, volumes, or mass.
- Complete dilution calculations.

There are several ways to express the amount of solute present in a solution. The **concentration** *of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution*. A **concentrated solution** *is one that has a relatively large amount of dissolved solute.* A **dilute solution** *is one that has a relatively small amount of dissolved solute*. However, these terms are relative, and we need to be able to express concentration in a more exact, quantitative manner. Still, concentrated and dilute are useful as terms to compare one solution to another (see figure below). Also, be aware that the terms "concentrate" and "dilute" can be used as verbs. If you were to heat a solution, causing the solvent to evaporate, you would be concentrating it, because the ratio of solute to solvent would be increasing. If you were to add more water to an aqueous solution, you would be diluting it because the ratio of solute to solvent would be decreasing.

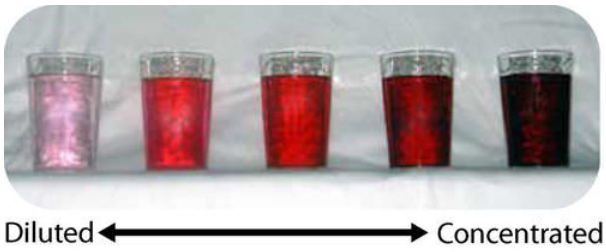


Figure 8.1.1: Solutions of a red dye in water from the most dilute (on the left) to the most concentrated (on the right).

Percent Concentration

One way to describe the concentration of a solution is by the percent of the solution that is composed of the solute. This percentage can be determined in one of three ways: (1) the mass of the solute divided by the mass of solution, (2) the volume of the solute divided by the volume of the solution, or (3) the mass of the solute divided by the volume of the solution. Because these methods generally result in slightly different vales, it is important to always indicate how a given percentage was calculated.

Mass Percent

When the solute in a solution is a solid, a convenient way to express the concentration is a mass percent (mass/mass), which is the grams of solute per $100\ \text{g}$ of solution.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \tag{3.4.1}$$

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $125\ \text{g}$ of water. The percent by mass would be calculated as follows:

$$\text{Percent by mass} = \frac{25\ \text{g sugar}}{125\ \text{g solution}} \times 100\% = 20\%\ \text{sugar} \tag{3.4.2}$$

Sometimes, you may want to make a particular amount of solution with a certain percent by mass and will need to calculate what mass of the solute is needed. For example, let's say you need to make $3.00 \times 10^3\ \text{g}$ of a sodium chloride solution that is 5.00% by mass. You can rearrange and solve for the mass of solute.

$$\%\ \text{by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \tag{3.4.3}$$

$$5.00\% = \frac{\text{mass of solute}}{3.00 \times 10^3\ \text{g solution}} \times 100\% \tag{3.4.4}$$

$$\text{mass of solute} = 150.\ \text{g} \tag{3.4.5}$$

You would need to weigh out $150\ \text{g}$ of NaCl and add it to $2850\ \text{g}$ of water. Notice that it was necessary to subtract the mass of the NaCl $(150\ \text{g})$ from the mass of solution $\left(3.00 \times 10^3\ \text{g}\right)$ to calculate the mass of the water that would need to be added.

Volume Percent

The percentage of solute in a solution can more easily be determined by volume when the solute and solvent are both liquids. The volume of the solute divided by the volume of the solution expressed as a percent, yields the percent by volume (volume/volume) of the solution. If a solution is made by taking $40.\ \text{mL}$ of ethanol and adding enough water to make $240.\ \text{mL}$ of solution, the percent by volume is:

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \tag{3.4.6}$$

$$= \frac{40\ \text{mL ethanol}}{240\ \text{mL solution}} \times 100\% \tag{3.4.7}$$

$$= 16.7\%\ \text{ethanol} \tag{3.4.8}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages (see figure below).

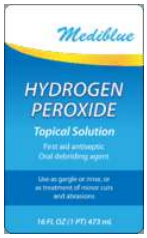


Figure 8.1.2: Hydrogen peroxide is commonly sold as a 3% by volume solution for use as a disinfectant.

It should be noted that, unlike in the case of mass, you cannot simply add together the volumes of solute and solvent to get the final solution volume. When adding a solute and solvent together, mass is conserved, but volume is not always conserved. In some cases, like in the example above, a solution was made by starting with $40\ \text{mL}$ of ethanol and adding enough water to make $240\ \text{mL}$ of solution. Simply mixing $40\ \text{mL}$ of ethanol and $200\ \text{mL}$ of water would not give you the same result, as the final volume would probably not be exactly $240\ \text{mL}$.

Mass-Volume Percent

The mass-volume percent is also used in some cases and is calculated in a similar way to the previous two percentages. The mass/volume percent is calculated by dividing the mass of the solute by the volume of the solution and expressing the result as a percent.

For example, if a solution is prepared from $10\ \text{NaCl}$ in enough water to make a $150\ \text{mL}$ solution, the mass-volume concentration is

$$\text{Mass-volume concentration} \frac{\text{mass solute}}{\text{volume solution}} \times 100\% \tag{3.4.9}$$

$$= \frac{10\ \text{g NaCl}}{150\ \text{mL solution}} \times 100\% \tag{3.4.10}$$

$$= 6.7\% \tag{3.4.11}$$

Parts per Million and Parts per Billion

Two other concentration units are parts per million and parts per billion. These units are used for very small concentrations of solute such as the amount of lead in drinking water. Understanding these two units is much easier if you consider a percentage as parts per hundred. Remember that 85% is the equivalent of 85 out of a hundred. A solution that is $15\ \text{ppm}$ is 15 parts solute per 1 million parts solution. A $22\ \text{ppb}$ solution is 22 parts solute per billion parts solution. While there are several ways of expressing two units of ppm and ppb, we will treat them as mg or μg of solutes per L solution, respectively.

For example, $32\ \text{ppm}$ could be written as $\frac{32\ \text{mg solute}}{1\ \text{L solution}}$ while $59\ \text{ppb}$ can be written as $\frac{59\ \mu\text{g solute}}{1\ \text{L solution}}$.

Molarity

Chemists primarily need the concentration of solutions to be expressed in a way that accounts for the number of particles present that could react according to a particular chemical equation. Since percentage measurements are based on either mass or volume, they are generally not useful for chemical reactions. A concentration unit based on moles is preferable. The **molarity** (M) *of a solution is the number of moles of solute dissolved in one liter of solution*. To calculate the molarity of a solution, you divide the moles of solute by the volume of the solution expressed in liters.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mol}}{\text{L}} \tag{3.4.12}$$

Note that the volume is in liters of solution and not liters of solvent. When a molarity is reported, the unit is the symbol M, which is read as "molar". For example, a solution labeled as $1.5\ \text{M}\ \text{NH}_3$ is a "1.5 molar solution of ammonia".

Example 8.1.1

A solution is prepared by dissolving $42.23\ \text{g}$ of NH_4Cl into enough water to make $500.0\ \text{mL}$ of solution. Calculate its molarity.

Solution:

Step 1: List the known quantities and plan the problem.

Known

- Mass of $\text{NH}_4\text{Cl} = 42.23\ \text{g}$
- Molar mass of $\text{NH}_4\text{Cl} = 53.50\ \text{g/mol}$
- Volume of solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$

Unknown

- Molarity $=?\ \text{M}$

The mass of the ammonium chloride is first converted to moles. Then, the molarity is calculated by dividing by liters. Note that the given volume has been converted to liters.

Step 2: Solve.

$$42.23\ \text{g}\ \text{NH}_4\text{Cl} \times \frac{1\ \text{mol}\ \text{NH}_4\text{Cl}}{53.50\ \text{g}\ \text{NH}_4\text{Cl}} = 0.7893\ \text{mol}\ \text{NH}_4\text{Cl} \tag{3.4.13}$$

$$\frac{0.7893\ \text{mol}\ \text{NH}_4\text{Cl}}{0.5000\ \text{L}} = 1.579\ \text{M} \tag{3.4.14}$$

Step 3: Think about your result.

The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain 1.579 moles of NH_4Cl. Having four significant figures is appropriate.



Figure 8.1.3: Volumetric flasks come in many sizes, each designed to prepare a different volume of solution.

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of moles of the solute does not change, but the total volume of the solution increases. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2 \tag{3.4.15}$$

Since the moles of solute in a solution is equal to the molarity multiplied by the volume in liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2 \tag{3.4.16}$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2 \tag{3.4.17}$$

Additionally, the concentration can be in any other unit as long as M_1 and M_2 are in the same unit.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl} \tag{3.4.18}$$

The solution has been diluted by a factor of five, since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value. Another common dilution problem involves deciding how much a highly concentrated solution is required to make a desired quantity of solution with a lower concentration. The highly concentrated solution is typically referred to as the stock solution.

Example 8.1.2

Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution:

Step 1: List the known quantities and plan the problem.

Known

- Stock $\mathrm{HNO_3}$ $(M_1) = 16\ \mathrm{M}$
- $V_2 = 8.00\ \mathrm{L}$
- $M_2 = 0.50\ \mathrm{M}$

Unknown

- Volume of stock $\mathrm{HNO_3}$ $(V_1) = ?\ \mathrm{L}$

The unknown in the equation is V_1, the necessary volume of the concentrated stock solution.

Step 2: Solve.

$$V_1 = \frac{M_2 \times V_2}{V_1} = \frac{0.50\ \mathrm{M} \times 8.00\ \mathrm{L}}{16\ \mathrm{M}} = 0.25\ \mathrm{L} = 250\ \mathrm{mL} \tag{3.4.19}$$

Step 3: Think about your result.

$250\ \mathrm{mL}$ of the stock $\mathrm{HNO_3}$ solution needs to be diluted with water to a final volume of $8.00\ \mathrm{L}$. The dilution from $16\ \mathrm{M}$ to $0.5\ \mathrm{M}$ is a factor of 32.

Equivalents

Concentration is important in healthcare because it is used in so many ways. It's also critical to use units with any values to ensure the correct dosage of medications or report levels of substances in blood, to name just two.

Another way of looking at concentration such as in IV solutions and blood is in terms of equivalents. One equivalent is equal to one mole of charge in an ion. The value of the equivalents is always positive regardless of the charge. For example, $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ both have 1 equivalent per mole.

Ion	Equivalents
$\mathrm{Na^+}$	1
$\mathrm{Mg^{2+}}$	2
$\mathrm{Al^{3+}}$	3
$\mathrm{Cl^-}$	1
$\mathrm{NO_3^-}$	1
$\mathrm{SO_4^{2-}}$	2

(3.4.20)

Equivalents are used because the concentration of the charges is important than the identity of the solutes. For example, a standard IV solution does not contain the same solutes as blood but the concentration of charges is the same.

Sometimes, the concentration is lower in which case milliequivalents (mEq) is a more appropriate unit. Just like metric prefixes used with base units, milli is used to modify equivalents so $1\ \mathrm{Eq} = 1000\ \mathrm{mEq}$.

Example 8.1.3

How many equivalents of $\mathrm{Ca^{2+}}$ are present in a solution that contains 3.5 moles of $\mathrm{Ca^{2+}}$?

Solution:

Use the relationship between moles and equivalents of $\mathrm{Ca^{2+}}$ to find the answer.

$$3.5\ \mathrm{mol} \cdot \frac{2\ \mathrm{Eq}}{1\ \mathrm{mol\ Ca^{2+}}} = 7.0\ \mathrm{Eq\ Ca^{2+}} \tag{3.4.21}$$

Example 8.1.4

A patient received $1.50\ \mathrm{L}$ of saline solution which has a concentration of $154\ \mathrm{mEq/L}$ $\mathrm{Na^+}$. What mass of sodium did the patient receive?

Solution:

Use dimensional analysis to set up the problem based on the values given in the problem, the relationship for $\mathrm{Na^+}$ and equivalents and the molar mass of sodium. Note that if this problem had a different ion with a different charge, that would need to be accounted for in the calculation.

$$1.50\ \text{L} \cdot \frac{154\ \text{mEq}}{1\ \text{L}} \cdot \frac{1\ \text{Eq}}{1000\ \text{mEq}} \cdot \frac{1\ \text{mol Na}^+}{1\ \text{Eq}} \cdot \frac{22.99\ \text{g}}{1\ \text{mol Na}^+} = 5.31\ \text{g Na}^+ \tag{3.4.22}$$

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3.5: Stoichiometry calculations with solutions

Learning Objective

- Apply concentration units as conversion factors.

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

$$0.108\ \cancel{L\ NaCl} \times \frac{0.887\ mol\ NaCl}{\cancel{L\ NaCl}} = 0.0958\ mol\ NaCl$$

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 3.5.1

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:

$$4.88\ \cancel{mol\ CuSO_4} \times \frac{1\ L}{2.35\ \cancel{mol}} = 2.08\ L\ of\ solution$$

Exercise 3.5.1

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer:

1.74 L

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

Example 3.5.2

What mass of solute is present in 0.765 L of 1.93 M NaOH?

Solution

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765\ \cancel{L} \times \frac{1.93\ \cancel{mol\ NaOH}}{\cancel{L\ solution}} \times \frac{40.0\ g\ NaOH}{1\ \cancel{mol\ NaOH}} = 59.1\ g\ NaOH$$

Exercise 3.5.2

What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

Answer

6.12 g

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)$$

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to liters of solution:

$$1.25\ \cancel{mol\ AgNO_3} \times \frac{1\ \cancel{mol\ CaCl_2}}{2\ \cancel{mol\ AgNO_3}} \times \frac{1L\ solution}{0.555\ \cancel{mol\ CaCl_2}} = 1.13\,L\,CaCl_2$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

Example 3.5.3

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3\,Ag\,(s) + Al(NO_3)_3\,(aq) \longrightarrow 3\,AgNO_3 + Al\,(s)$$

Solution

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66\ \cancel{g\ Ag} \times \frac{1\ \cancel{mol\ Ag}}{107.97\ \cancel{g\ Ag}} \times \frac{1\ \cancel{mol\ Al(NO_3)_3}}{3\ \cancel{mol\ Ag}} \times \frac{1L\ solution}{0.0995\ \cancel{mol\ Al(NO_3)_3}} = 0.114\,L$$

The strikeouts show how the units cancel.

Exercise 3.5.3

What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4(s)$ according to the following chemical equation?

$$H_2C_2O_4\,(s) + 2\,NaOH\,(aq) \longrightarrow Na_2C_2O_4\,(aq) + 2\,H_2O(\ell)$$

Answer:

0.777 L

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

Example 3.5.4

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of $FeCl_3$. The student carefully adds 0.1074 M $Na_2C_2O_4$ until all the $Fe^{3+}(aq)$ has precipitated as $Fe_2(C_2O_4)_3(s)$. Using a precisely measured tube called a burette, the student finds that 9.04 mL of the $Na_2C_2O_4$ solution was added to completely precipitate the $Fe^{3+}(aq)$. What was the concentration of the $FeCl_3$ in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2\,FeCl_3\,(aq) + 3\,Na_2C_2O_4\,(aq) \longrightarrow Fe_2(C_2O_4)_3\,(s) + 6\,NaCl\,(aq)$$

Solution

First we need to determine the number of moles of $Na_2C_2O_4$ that reacted. We will convert the volume to liters and then use the concentration of the solution as a conversion factor:

$$9.04\,\cancel{mL} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{0.1074 mol\,Na_2C_2O_4}{\cancel{L}} = 0.000971\,mol\,Na_2C_2O_4$$

Now we will use the balanced chemical equation to determine the number of moles of Fe^{3+}(aq) that were present in the initial aliquot:

$$0.000971\,\cancel{mol\,Na_2C_2O_4} \times \frac{2 mol\,FeCl_3}{3\,\cancel{mol Na_2C_2O_4}} = 0.000647 mol\,FeCl_3$$

Then we determine the concentration of $FeCl_3$ in the original solution. Converting 10.00 mL into liters (0.01000 L), we use the definition of molarity directly:

$$M = \frac{mol}{L} = \frac{0.000647 mol\,FeCl_3}{0.01000 L} = 0.0647 M\,FeCl_3$$

Exercise 3.5.4

A student titrates 25.00 mL of H_3PO_4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H_3PO_4?

$$H_3PO_4\,(aq) + 3\,KOH\,(aq) \longrightarrow K_3PO_4\,(aq) + 3\,H_2O$$

Answer:

0.0711 M



Figure **3.5.1** Titration © Thinkstock. When a student performs a titration, a measured amount of one solution is added to another reactant.

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

Example 3.5.5

H_2O_2 is used to determine the amount of Mn according to this balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,H_2O_2(aq) + 6\,H^+(aq) \longrightarrow 2\,Mn_2^+(aq) + 5\,O_2(g) + 8\,H_2O(\ell)$$

What mass of 3.00% m/m H_2O_2 solution is needed to react with 0.355 mol of MnO_4^-(aq)?

Solution

Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of H_2O_2 and then convert to find the mass of H_2O_2. Knowing that the H_2O_2 solution is 3.00% by mass, we can determine the mass of solution needed:

$$0.355\ \cancel{mol\ MnO_4^-} \times \frac{5\ \cancel{mol\ H_2O_2}}{2\ \cancel{mol\ MnO_4^-}} \times \frac{34.02\ \cancel{g\ H_2O_2}}{\cancel{mol\ H_2O_2}} \times \frac{100 g\ solution}{3\ \cancel{g\ H_2O_2}} = 1006 g\ sol$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of H_2O_2, and the third conversion factor comes from the definition of percentage concentration by mass.

Exercise 3.5.5

Use the balanced chemical reaction for MnO_4^- and H_2O_2 to determine what mass of O_2 is produced if 258 g of 3.00% m/m H_2O_2 is reacted with MnO_4^-.

Answer

7.28 g

Summary

Know how to apply concentration units as conversion factors.

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3.6: Colligative Properties of Solutions

Learning Objective

- Name the four colligative properties.
- Calculate changes in vapor pressure, melting point, and boiling point of solutions.
- Calculate the osmotic pressure of solutions.

The properties of solutions are very similar to the properties of their respective pure solvents. This makes sense because the majority of the solution *is* the solvent. However, some of the properties of solutions differ from pure solvents in measurable and predictable ways. The differences are proportional to the fraction that the solute particles occupy in the solution. These properties are called **colligative properties**; the word *colligative* comes from the Greek word meaning "related to the number," implying that these properties are related to the number of solute particles, not their identities.

Before we introduce the first colligative property, we need to introduce a new concentration unit. The **mole fraction** of the *ith* component in a solution, χ_i, is the number of moles of that component divided by the total number of moles in the sample:

$$\chi_i = \frac{moles\ of\ ith\ component}{total\ moles}$$

(χ is the lowercase Greek letter chi.) The mole fraction is always a number between 0 and 1 (inclusive) and has no units; it is just a number.

Example 3.6.1: Hydrocarbon Solution

A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. What is the mole fraction of $C_{10}H_8$ in the solution?

Solution

We need to determine the number of moles of each substance, add them together to get the total number of moles, and then divide to determine the mole fraction of $C_{10}H_8$. The number of moles of $C_{10}H_8$ is as follows:

$$12.0g\ C_{10}H_8 \times \frac{1mol\ C_{10}H_8}{128.10g\ C_{10}H_8} = 0.0936\ mol\ C_{10}H_8$$

The number of moles of C_6H_6 is as follows:

$$45.0g\ C_6H_6 \times \frac{1mol\ C_6H_6}{78.12g\ C_6H_6} = 0.576\ mol\ C_6H_6$$

The total number of moles is

$$0.0936\ mol + 0.576\ mol = 0.670\ mol$$

Now we can calculate the mole fraction of $C_{10}H_8$:

$$\chi_{C_{10}H_8} = \frac{0.0936mol}{0.670mol} = 0.140$$

The mole fraction is a number between 0 and 1 and is unit-less.

Exercise 3.6.1

A solution is made by mixing 33.8 g of CH_3OH in 50.0 g of H_2O. What is the mole fraction of CH_3OH in the solution?

Answer

0.275

A useful thing to note is that the sum of the mole fractions of all substances in a mixture equals 1. Thus the mole fraction of C_6H_6 in Example **3.6.1** could be calculated by evaluating the definition of mole fraction a second time, or—because there are only two

substances in this particular mixture—we can subtract the mole fraction of the $C_{10}H_8$ from 1 to get the mole fraction of C_6H_6.

Vapor pressure depression

Now that this new concentration unit has been introduced, the first colligative property can be considered. As mentioned in Chapter 10, all pure liquids have a characteristic vapor pressure in equilibrium with the liquid phase, the partial pressure of which is dependent on temperature. Solutions, however, have a lower vapor pressure than the pure solvent has, and the amount of lowering is dependent on the fraction of solute particles, as long as the solute itself does not have a significant vapor pressure (the term *nonvolatile* is used to describe such solutes). This colligative property is called **vapor pressure depression** (or *lowering*). The actual vapor pressure of the solution can be calculated as follows:

$$P_{soln} = \chi_{solv} P^*_{solv}$$

where P_{soln} is the vapor pressure of the solution, χ_{solv} is the mole fraction of the solvent particles, and P^*_{solv} is the vapor pressure of the pure solvent at that temperature (which is data that must be provided). This equation is known as **Raoult's law** (the approximate pronunciation is *rah-OOLT*). Vapor pressure depression is rationalized by presuming that solute particles take positions at the surface in place of solvent particles, so not as many solvent particles can evaporate.

Example 3.6.2: Vapor Pressure Reduction

A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. If the vapor pressure of pure C_6H_6 is 95.3 torr, what is the vapor pressure of the solution?

Solution

This is the same solution that was in Example 15, but here we need the mole fraction of C_6H_6. The number of moles of $C_{10}H_8$ is as follows:

$$12.0 g\, C_{10}H_8 \times \frac{1 mol\, C_{10}H_8}{128.10 g\, C_{10}H_8} = 0.0936\, mol\, C_{10}H_8$$

The number of moles of C_6H_6 is as follows:

$$45.0 g\, C_6H_6 \times \frac{1 mol\, C_6H_6}{78.12 g\, C_6H_6} = 0.576\, mol\, C_6H_6$$

So the total number of moles is

$$0.0936 \text{ mol} + 0.576 \text{ mol} = 0.670 \text{ mol}$$

Now we can calculate the mole fraction of C_6H_6:

$$\chi_{C_{10}H_8} = \frac{0.576 mol}{0.670 mol} = 0.860$$

(The mole fraction of $C_{10}H_8$ calculated in Example 15 plus the mole fraction of C_6H_6 equals 1, which is mathematically required by the definition of mole fraction.) Now we can use Raoult's law to determine the vapor pressure in equilibrium with the solution:

$$P_{soln} = (0.860)(95.3 \text{ torr}) = 82.0 \text{ torr}$$

The solution has a lower vapor pressure than the pure solvent.

Exercise 3.6.2

A solution is made by mixing 33.8 g of $C_6H_{12}O_6$ in 50.0 g of H_2O. If the vapor pressure of pure water is 25.7 torr, what is the vapor pressure of the solution?

Answer

24.1 torr

Boiling point elevation

Two colligative properties are related to solution concentration as expressed in molality. As a review, recall the definition of molality:

$$molality = \frac{moles\ solute}{kilograms\ solvent}$$

Because the vapor pressure of a solution with a nonvolatile solute is depressed compared to that of the pure solvent, it requires a higher temperature for the solution's vapor pressure to reach 1.00 atm (760 torr). Recall that this is the definition of the normal boiling point: the temperature at which the vapor pressure of the liquid equals 1.00 atm. As such, the normal boiling point of the solution is higher than that of the pure solvent. This property is called **boiling point elevation**.

The change in boiling point (ΔT_b) is easily calculated:

$$\Delta T_b = mK_b$$

where m is the molality of the solution and K_b is called the **boiling point elevation constant,** which is a characteristic of the solvent. Several boiling point elevation constants (as well as boiling point temperatures) are listed in Table **3.6.1**.

Table **3.6.1**: Boiling Point Data for Various Liquids

Liquid	Boiling Point (°C)	K_b (°C/m)
$HC_2H_3O_2$	117.90	3.07
C_6H_6	80.10	2.53
CCl_4	76.8	4.95
H_2O	100.00	0.512

Remember that what is initially calculated is the *change* in boiling point temperature, not the new boiling point temperature. Once the change in boiling point temperature is calculated, it must be added to the boiling point of the pure solvent—because boiling points are always elevated—to get the boiling point of the solution.

Example 3.6.3

What is the boiling point of a 2.50 m solution of $C_6H_4Cl_2$ in CCl_4? Assume that $C_6H_4Cl_2$ is not volatile.

Solution

Using the equation for the boiling point elevation,

$$\Delta T_b = (2.50\ m)(4.95°C/m) = 12.4°C$$

Note how the molality units have canceled. However, we are not finished. We have calculated the change in the boiling point temperature, not the final boiling point temperature. If the boiling point goes up by 12.4°C, we need to add this to the normal boiling point of CCl_4 to get the new boiling point of the solution:

$$T_{BP} = 76.8°C + 12.4°C = 89.2°C$$

The boiling point of the solution is predicted to be 89.2°C.

Exercise 3.6.3

What is the boiling point of a 6.95 m solution of $C_{12}H_{22}O_{11}$ in H_2O?

Answer

103.6°C

Freezing point depression

The boiling point of a solution is higher than the boiling point of the pure solvent, but the opposite occurs with the freezing point. The freezing point of a solution is lower than the freezing point of the pure solvent. Think of this by assuming that solute particles interfere with solvent particles coming together to make a solid, so it takes a lower temperature to get the solvent particles to solidify. This is called **freezing point depression**.

The equation to calculate the change in the freezing point for a solution is similar to the equation for the boiling point elevation:

$$\Delta T_f = mK_f$$

where m is the molality of the solution and K_f is called the **freezing point depression constant,** which is also a characteristic of the solvent only. Several freezing point depression constants (as well as freezing point temperatures) are listed in Table **3.6.2**.

Table **3.6.2**: Freezing Point Data for Various Liquids

Liquid	Freezing Point (°C)	K_f (°C/m)
$HC_2H_3O_2$	16.60	3.90
C_6H_6	5.51	4.90
C_6H_{12}	6.4	20.2
$C_{10}H_8$	80.2	6.8
H_2O	0.00	1.86

Remember that this equation calculates the change in the freezing point, not the new freezing point. What is calculated needs to be subtracted from the normal freezing point of the solvent, because freezing points always decrease.

Example **3.6.4**: Freezing Point Reduction

What is the freezing point of a 1.77 m solution of CBr_4 in C_6H_6?

Solution

We use the equation to calculate the change in the freezing point and then subtract this number from the normal freezing point of C_6H_6 to get the freezing point of the solution:

$$\Delta T_f = (1.77\ m)(4.90°C/m) = 8.67°C$$

Now we subtract this number from the normal freezing point of C_6H_6, which is 5.51°C:

$$5.51 - 8.67 = -3.16°C$$

The freezing point of the solution is −3.16°C.

Exercise **3.6.4**

What is the freezing point of a 3.05 m solution of CBr_4 in $C_{10}H_8$?

Answer

59.5°C

Freezing point depression is one colligative property that we use in everyday life. Many antifreezes used in automobile radiators use solutions that have a lower freezing point than normal so that automobile engines can operate at subfreezing temperatures. We also take advantage of freezing point depression when we sprinkle various compounds on ice to thaw it in the winter for safety (Figure **3.6.1**). The compounds make solutions that have a lower freezing point, so rather than forming slippery ice, any ice is liquefied and runs off, leaving a safer pavement behind.



Figure **3.6.1**: Salt and Safety © Thinkstock. Salt or other compounds take advantage of the freezing point depression to minimize the formation of ice on sidewalks and roads, thus increasing safety.

Osmotic pressure

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane. Consider the system in Figure **3.6.2**.

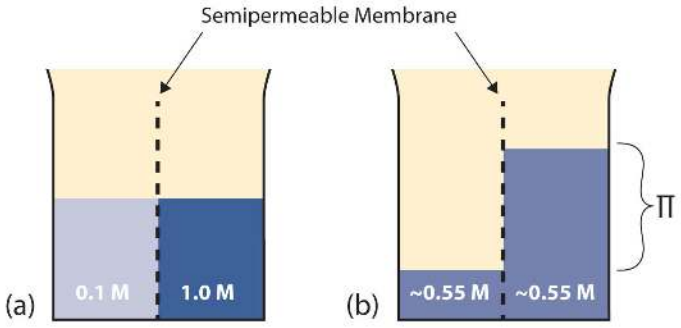


Figure **3.6.2**: Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure.

a. A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until the concentrations are equalized, as in Figure **3.6.2**.
b. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference Π on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

The osmotic pressure of a solution is easy to calculate:

$$\Pi = MRT$$

where Π is the osmotic pressure of a solution, M is the molarity of the solution, R is the ideal gas law constant, and T is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6.

Example 3.6.5: Osmotic Pressure

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

Solution

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for R:

$$\prod = (0.333M)\left(0.08205\frac{L.atm}{mol.K}\right)(298K)$$

The units may not make sense until we realize that molarity is defined as moles per liter:

$$\prod = \left(0.333\frac{mol}{L}\right)\left(0.08205\frac{L.atm}{mol.K}\right)(298K)$$

Now we see that the moles, liters, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving,

$$\Pi = 8.14 \text{ atm}$$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

Exercise 3.6.5

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

Answer

1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum; otherwise there may be negative consequences. Figure **3.6.3** shows three red blood cells:

- a healthy red blood cell
- a red blood cell that has been exposed to a lower concentration than normal blood serum (a so-called *hypotonic* solution); the cell has plumped up as solvent moves into the cell to dilute the solutes inside.
- a red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*); water leaves the red blood cell, so it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.

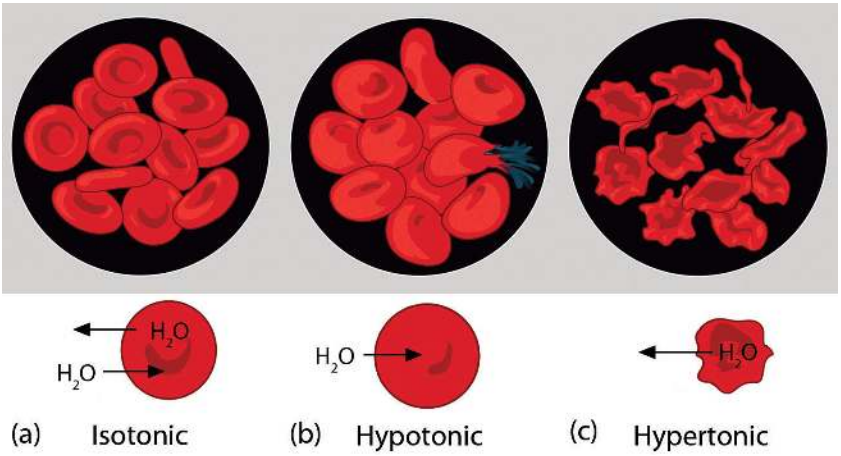


Figure **3.6.3**: Osmotic Pressure and Red Blood Cells. (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects.

Osmotic pressure is also the reason you should not drink seawater if you're stranded in a lifeboat on an ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is OK to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important in getting water to the tops of tall trees, in addition to capillary action.

Summary

- Colligative properties depend only on the number of dissolved particles (that is—the concentration), not their identity.
- Raoult's law is concerned with the vapor pressure depression of solutions.
- The boiling points of solutions are always higher, and the freezing points of solutions are always lower, than those of the pure solvent.
- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane and is an important biological issue.

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3.7: Colligative Properties of Ionic Solutes

Learning Objective

- Determine the colligative properties of solutions of ionic solutes.

Previously, we considered the colligative properties of solutions with molecular solutes. What about solutions with ionic solutes? Do they exhibit colligative properties?

There is a complicating factor: ionic solutes separate into ions when they dissolve. This increases the total number of particles dissolved in solution and *increases the impact on the resulting colligative property*. Historically, this greater-than-expected impact on colligative properties was one main piece of evidence for ionic compounds separating into ions (increased electrical conductivity was another piece of evidence).

For example, when NaCl dissolves, it separates into two ions:

$$\mathrm{NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)}$$

This means that a 1 M solution of NaCl actually has a net particle concentration of 2 M. The observed colligative property will then be twice as large as expected for a 1 M solution.

It is easy to incorporate this concept into our equations to calculate the respective colligative property. We define the **van 't Hoff factor** (i) as the number of particles each solute formula unit breaks apart into when it dissolves. Previously, we have always tacitly assumed that the van 't Hoff factor is simply 1. But for some ionic compounds, i is not 1, as shown in Table **3.7.1**.

Table **3.7.1** Ideal van 't Hoff Factors for Ionic Compounds

Compound	i
NaCl	2
KBr	2
$LiNO_3$	2
$CaCl_2$	3
$Mg(C_2H_3O_2)_2$	3
$FeCl_3$	4
$Al_2(SO_4)_3$	5

The ideal van 't Hoff factor is equal to the number of ions that form when an ionic compound dissolves.

Example 3.7.1

Predict the van 't Hoff factor for $Sr(OH)_2$.

Solution

When $Sr(OH)_2$ dissolves, it separates into one Sr^{2+} ion and two OH^- ions:

$$\mathrm{Sr(OH)_2 \rightarrow Sr^{2+}(aq) + 2\,OH^-(aq)}$$

Because it breaks up into three ions, its van 't Hoff factor is 3.

Exercise 3.7.1

What is the van 't Hoff factor for $Fe(NO_3)_3$?

Answer

4

It is the "ideal" van 't Hoff factor because this is what we expect from the ionic formula. However, this factor is usually correct only for dilute solutions (solutions less than 0.001 M). At concentrations greater than 0.001 M, there are enough interactions between ions of opposite charge that the net concentration of the ions is less than expected—sometimes significantly. The actual van 't Hoff factor is thus less than the ideal one. Here, we will use ideal van 't Hoff factors.

Revised equations to calculate the effect of ionization are then easily produced:

$$\Delta T_b = imK_b$$

$$\Delta T_f = imK_g$$

$$\Pi = iMRT$$

where all variables have been previously defined. To calculate vapor pressure depression according to Raoult's law, the mole fraction of solvent particles must be recalculated to take into account the increased number of particles formed on ionization.

Example 3.7.2

Determine the freezing point of a 1.77 *m* solution of NaCl in H_2O.

Solution

For NaCl, we need to remember to include the van 't Hoff factor, which is 2. Otherwise, the calculation of the freezing point is straightforward:

$$\Delta T_f = (2)(1.77\,m)(1.86\,°C/m) = 6.58°C$$

This represents the change in the freezing point, which is decreasing. So we have to subtract this change from the normal freezing point of water, 0.00°C:

0.00 − 6.58 = −6.58°C

Exercise 3.7.2

Determine the boiling point of a 0.887 m solution of $CaCl_2$ in H_2O.

Answer

101.36 °C

Food and Drink App: Salting Pasta Cooking Water

When cooking dried pasta, many recipes call for salting the water before cooking the pasta. Some argue—with colligative properties on their side—that adding salt to the water raises the boiling point, thus cooking the pasta faster. Is there any truth to this?



Figure **3.7.1**: Cooking dried pasta. Why do so many recipes call for adding salt to water when boiling pasta? Is it to raise the boiling temperature of the water? (Public Domain; Jan Vašek via pixabay)

To judge the veracity of this claim, we can calculate how much salt should be added to the water to raise the boiling temperature by 1.0°C, with the presumption that dried pasta cooks noticeably faster at 101°C than at 100°C (although a 1° difference may make only a negligible change in cooking times). We can calculate the molality that the water should have:

$$1.0°C = m(0.512°C/m)m = 1.95$$

We have ignored the van 't Hoff factor in our estimation because this obviously is not a dilute solution. Let us further assume that we are using 4 L of water (which is very close to 4 qt, which in turn equals 1 gal). Because 4 L of water is about 4 kg (it is actually slightly less at 100°C), we can determine how much salt (NaCl) to add:

$$4\ \cancel{kg\ H_2O} \times \frac{1.95\ \cancel{mol\ NaCl}}{\cancel{kg\ H_2O}} \times \frac{58.5g\ NaCl}{1\ \cancel{mol\ NaCl}} = 456.3g\ NaCl$$

This is just over 1 lb of salt and is equivalent to nearly 1 cup in the kitchen. In your experience, do you add almost a cup of salt to a pot of water to make pasta? Certainly not! A few pinches, perhaps one-fourth of a teaspoon, but not almost a cup! It is obvious that the little amount of salt that most people add to their pasta water is not going to significantly raise the boiling point of the water.

So why do people add some salt to boiling water? There are several possible reasons, the most obvious of which is taste: adding salt adds a little bit of salt flavor to the pasta. It cannot be much because most of the salt remains in the water, not in the cooked pasta. However, it may be enough to detect with our taste buds. The other obvious reason is habit; recipes tell us to add salt, so we do, even if there is little scientific or culinary reason to do so.

Summary

For ionic solutes, the calculation of colligative properties must include the fact that the solutes separate into multiple particles when they dissolve. The equations for calculating colligative properties of solutions of ionic solvents include the van 't Hoff factor, *i*.

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3.8: Colloids and Suspensions

Learning Outcomes

- Describe the properties of a suspension.
- Describe the properties of a colloid.
- Distinguish among suspensions. colloids, and solutions.

Suspensions

Take a glass of water and throw in a handful of sand or dirt. Stir it and stir it and stir it. Have you made a solution? Sand and dirt do not dissolve in water, and, though it may look homogenous for a few moments, the sand or dirt gradually sinks to the bottom of the glass (see figure below). Some medications are delivered as suspensions and must be mixed well before the doses measured to make sure the patient is receiving the correct amount of medication.



Figure 3.8.1: A mixture of sand and water forms a suspension.

A **suspension** *is a heterogeneous mixture in which some of the particles settle out of the mixture upon standing*. The particles in a suspension are far larger than those of a solution, so gravity is able to pull them down out of the dispersion medium (water). The diameter for the dispersed particles in a suspension, such as the sand in the suspension described above, is typically at least 1000 times greater than those in a solution. Unlike a solution, the dispersed particles can be separated from the dispersion medium by filtering. Suspensions are considered heterogeneous because the different substances in the mixture will not remain uniformly distributed if they are not actively being mixed.

Colloids

A colloid is a heterogeneous mixture in which the dispersed particles are intermediate in size between those of a solution and a suspension. The particles are spread evenly throughout the dispersion medium, which can be a solid, liquid, or gas. Because the dispersed particles of a colloid are not as large as those of a suspension, they do not settle out upon standing. The table below summarizes the properties and distinctions between solutions, colloids, and suspensions.

Table 3.8.1: Properties of Solutions, Colloids, and Suspensions

Solution	Colloids	Suspensions
Homogeneous	Heterogeneous	Heterogeneous
Particle size: **0.01-1 nm**; atoms, ions or molecules	Particle size: **1-1000 nm**, dispersed; large molecules or aggregates	Particle size: over **1000 nm**, suspended: large particles or aggregates
Do not separate on standing	Do not separate on standing	Particles settle out
Cannot be separated by filtration	Cannot be separated by filtration	Can be separated by filtration
Do not scatter light	Scatter light (Tyndall effect)	May either scatter light or be opaque

Colloids are unlike solutions because their dispersed particles are much larger than those of a solution. The dispersed particles of a colloid cannot be separated by filtration, but they scatter light, a phenomenon called the Tyndall effect.

Tyndall Effect

Colloids are often confused with true homogenous solutions because the individual dispersed particles of a colloid cannot be seen. When light is passed through a true solution, the dissolved particles are too small to deflect the light. However, the dispersed particles of a colloid, being larger, do deflect light (see figure below). The **Tyndall effect** *is the scattering of visible light by colloidal particles*. You have undoubtedly "seen" a light beam as it passes through fog, smoke, or a scattering of dust particles suspended in air. All three are examples of colloids. Suspensions may scatter light, but if the number of suspended particles is sufficiently large, the suspension may simply be opaque, and the light scattering will not occur.



Figure **3.8.2**: Light passes through a colorless solution and is not scattered. When it passes through a diluted milk solution, the light is scattered by colloidal particles, an observation of the Tyndall effect. The Tyndall effect allows sunlight to be seen as it passes through a fine mist.

Examples of Colloids

Listed in the table below are examples of colloidal systems, most of which are very familiar. Some of these are shown below (see figure below). The dispersed phase describes the particles, while the dispersion medium is the material in which the particles are distributed.

Table **3.8.2**: Classes of Colloids

Class of Colloid	Dispersed Phase	Dispersion Medium	Examples
Sol and gel	solid	liquid	paint, jellies, blood, gelatin, mud
Solid aerosol	solid	gas	smoke, dust in air
Solid emulsion	liquid	solid	cheese, butter
Liquid emulsion	liquid	liquid	milk, mayonnaise
Liquid aerosol	liquid	gas	fog, mist, clouds, aerosol spray
Foam	gas	solid	marshmallow
Foam	gas	liquid	whipped cream, shaving cream



Figure **3.8.3**: Some common colloids (A) gelatin dessert, (B) smoke (solid aerosol), (C) butter (solid emulsion), (D) mayonnaise (liquid emulsion), (E) fog (liquid aerosol), (F) marshmallows (foam), (G) whipped cream (foam)

Emulsions

Butter and mayonnaise are examples of a class of colloids called emulsions. An **emulsion** *is a colloidal dispersion of a liquid in either a liquid or a solid.* A stable emulsion requires an emulsifying agent to be present. Mayonnaise is made in part of oil and vinegar. Since oil is nonpolar, and vinegar is a polar aqueous solution, the two do not mix and would quickly separate into layers. However, the addition of egg yolk causes the mixture to become stable and not separate. Egg yolk is capable of interacting with both the polar vinegar and the nonpolar oil. The egg yolk is called the emulsifying agent. Soap acts as an emulsifying agent because one end of a soap molecule is polar, and the other end is nonpolar. This allows the grease to be removed from your hands or your clothing by washing with soapy water.

Supplemental Resources

- Types of Mixtures - Solutions, Suspensions, Colloids: www.edinformatics.com/math_sc.../mixtures.html

Contributors and Attributions

-
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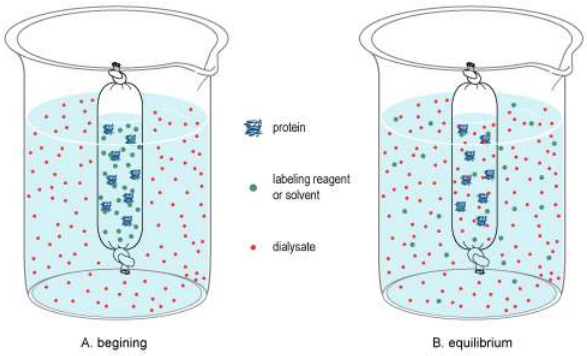
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3.9: Dialysis

Dialysis is the separation of colloids from dissolved ions or molecules of small dimensions, or crystalloid, in a solution. A **colloid** is any substance that is made of particles that are of an extremely small size: larger than atoms but generally have the size of 10^{-7} cm ranging to 10^{-3} cm. A **crystalloid** is a substance that has some or all of the properties of a crystal or a substance that forms a true solution and diffuses through a membrane by dialysis. Dialysis is a process that is like osmosis. Osmosis is the process in which there is a diffusion of a solvent through a semipermeable membrane.

Introduction

In 1861, chemist Thomas Graham (how developed Graham's Law) used the process of dialysis, a process used to separate colloidal particles from dissolved ions or molecules. Dialysis is possible because of the *unequal rates of diffusion* through a **semipermeable membrane**. A semipermeable membrane is a membrane that lets some molecules to pass through it while not letting others (Figure **3.9.1**). Examples of semipermeable membranes include parchment and cellophane.



Another way to think of a semipermeable membrane is to think of a net like object that traps larger objects, but lets smaller object pass through because they can pass through the holes in the net.



Video* 3.9.1*: *Osmotic Pressure Dialysis Tubing*

When a colloidal mixture is places in a semipermeable membrane, which is then placed in an aqueous solution or pure water, dissolved ions and small molecules are allowed to pass through this membrane. This causes colloidal particles to stay in the membrane, because these particles are unable to pass through the small pores of the membrane.

The Rate of Dialysis

Dialysis is not a quick process; the rate of dialysis depends on the speed of the unequal diffusion rates between the crystalloids and the colloids and the differences in particle size. The rate of dialysis can be changed through **heating**, or if the crystalloids are charged, then **applying an electric field**, called electrodialysis. Electrodialysis is the type of dialysis in which electrodes are placed

on the sides of the membrane. In this way, positive ions can pass through one side of this membrane while the negatively charged ions can pass through the other side of the membrane. This causes acceleration in the process of dialysis.

Hemodialysis

Hemodialysis is a method in which kidney failure is treated with the process of dialysis. In hemodialysis, blood is removed, purified through dialysis, and returned to the bloodstream. In kidney failure, there is a retention of salts and water, urea, and metabolic acids. The patient is then connected to a dialysis machine, which is also called a hemodialyzer. The blood flows through small channels made of semipermeable membranes (Figure **3.9.2**). The dissolved substances like urea and salts pass through a sterile solution. Compounds like sugar and amino acids are added to the sterile solution. The dialysis solution is on the other side of the membranes, and the molecules flow through the membranes. The molecules diffuse from a higher concentration to low concentration area. The concentrations of molecules needed to be removed from the blood are zero in the dialysis fluid.

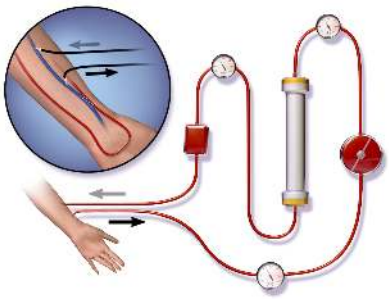


Figure **3.9.2**: (left) Scheme of semipermeable membrane during hemodialysis, where blood is red, dialysing fluid is blue, and the membrane is yellow. from Wikipedia (Freemesm). (right) Hemodialysis setup. Blausen.com staff. "Blausen gallery 2014". Wikiversity Journal of Medicine. DOI:10.15347/wjm/2014.010. ISSN 20018762. See a full animation of this medical topic.

The process of hemodialysis helps many patients who have kidney failure because a person who suffers from kidney failure are at great risk, because someone who has complete kidney failure will need a kidney transplant within two weeks, or else he/she will face death. Between the time that the person finds a suitable kidney to be transplanted, the hemodialyzer comes into great help in facing the fight against death.

References

1. Petrucci, et al. *General Chemistry Principles & Modern Applications*. 9th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2007.
2. Sadava, et al. *Life: The Science of Biology*. 8th ed. New York, NY. W.H. Freeman and Company, 2007.

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CHAPTER OVERVIEW

4: Thermochemistry and Thermodynamics

4.1: Heat
4.2: Bond Energies and Chemical Reactions. Endothermic and Exothermic Reactions.
4.3: Exothermic and Endothermic Processes
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4.5: Specific Heat Calculations
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4.1: Heat

Blacksmiths heat solid iron in order to shape it into a variety of different objects. Iron is a rigid, solid metal. At room temperature, it is extremely difficult to bend iron. However, when heated to a high enough temperature, iron can be easily worked. The heat energy in the forge is transferred to the metal, making the iron atoms vibrate more and move around more readily.

Heat is energy that is transferred from one object or substance to another because of a difference in temperature between the two. Heat always flows from an object at a higher temperature to an object at a lower temperature (see figure below). The flow of heat will continue until the two objects are at the same temperature.

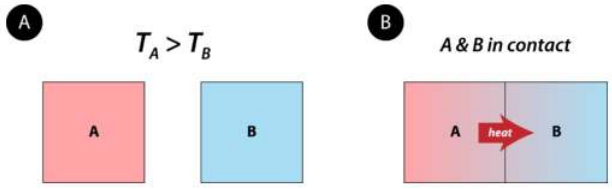


Figure* 4.1.1*: *Object A starts with a higher temperature than object B. No heat flows when the objects are isolated from each other. When brought into contact, heat flows from A to B until the temperatures of the two objects are the same.*

Thermochemistry is the study of energy changes that occur during chemical reactions and during changes of state. When chemical reactions occur, some chemical bonds are broken, while new chemical bonds form. As a result of the rearrangement of atoms, the total chemical potential energy of the system either increases or decreases.

Summary

- Heat is transferred energy from a site of higher energy to a site of lower energy.
- Thermochemistry is the study of energy changes that occur during chemical reactions and during changes of state.

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4.2: Bond Energies and Chemical Reactions. Endothermic and Exothermic Reactions.

Learning Objectives

The Learning Objectives of this Module are to:

- Define *bond energy*.
- Calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

What happens when you take a basketball, place it halfway up a playground slide, and then let it go? The basketball rolls down the slide. What happens if you do it again? Does the basketball roll down the slide? It should.

If you were to perform this experiment over and over again, do you think the basketball would ever roll *up* the slide? Probably not. Why not? Well, for starters, in all of our experience, the basketball has always moved to a lower position when given the opportunity. The gravitational attraction of Earth exerts a force on the basketball, and given the chance, the basketball will move down. We say that the basketball is going to a lower *gravitational potential energy*. The basketball can move up the slide, but only if someone exerts some effort (that is, work) on the basketball. A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

Bond Energy

A similar statement can be made about atoms in compounds. Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process, just as with the basketball. If we put energy into a molecule, we can cause its bonds to break, separating a molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the bond energy, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term *bond energy* is usually used to describe the strength of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. Table **4.2.1** lists the approximate bond energies of various covalent bonds.

Table **4.2.1**: Approximate Bond Energies

Bond	Bond Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200
N–H	93
H–H	105
Br-Br	46
Cl–Cl	58
O–H	110
O=O	119
H–Br	87
H–Cl	103

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The enthalpy change, for a given reaction can be calculated using the bond energy values from Table **4.2.1**.

Enthalpy Change or Heat of Reaction, Δ*H*

Energy changes in chemical reactions are usually measured as changes in enthalpy. In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

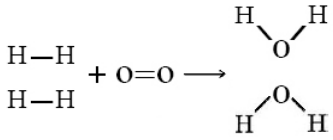
$$\text{enthalpy change} \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

The ≈ sign is used because we are adding together *average* bond energies (i.e., over many different molecules). Hence, this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas (H_2) with 1 mol of oxygen gas (O_2) to give 2 mol water:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

or shown graphically:



with these average bond energies involved:

- **H–H** = 105 kcal/mol
- **O=O** = 119 kcal/mol

- **O–H** = 110 kcal/mol

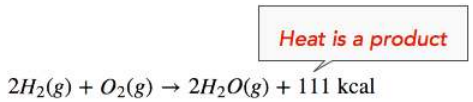
In this reaction, 2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated and calculated as follows:

2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H2O) are formed. The energy changes can be tabulated and calculated as follows:

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
2 H–H	2 mol x 105 kcal/mol = 210 kcal	4 O–H	4 mols x 110 kcal/mol = 440 kcal
1 O=O	1 mol x 119 kcal/mol = 119 kcal		
	Total = 329 kcal		**Total** = 440 kcal

$$\begin{aligned}\Delta H &\approx \sum(\text{bonds broken}) - \sum(\text{bonds formed}) \\ &\approx 329\ \text{kcal} - 440\ \text{kcal} \\ &\approx -111\ \text{kcal}\end{aligned}$$

The enthalpy change (ΔH) of the reaction is approximately −111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes. This excess energy is **released** as heat, so the reaction is **exothermic**. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:



We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \quad \Delta H = -111\ \text{kcal}$$

Example 4.2.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond energies of these bonds from Table **4.2.1**:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

Solutions to Example 7.4.1

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
1 H–H	1 mol x 105 kcal/mol = 105 kcal	2 H–*Br*	2 mols x 87 kcal/mol = 174 kcal
1 Br–Br	1 mol x 46 kcal/mol = 46 kcal		
	Total = 151 kcal		**Total** = 174 kcal

$$\Delta H \approx 151 \text{ kcal} - 174 \text{ kcal}$$
$$\approx -23 \text{ kcal}$$

Step 5- Since ΔH is negative (−23 kcal), the reaction is *exothermic*.

4.2.1 Exercise

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

Is the reaction written above exothermic or endothermic? Explain.

Answer

ΔH = −43 kcal

Since ΔH is negative (−43 kcal), the reaction is *exothermic*.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. **Endothermic** reactions require energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (ΔH is positive). As discussed in the previous section, in an **exothermic** reaction, heat is released (considered a product) and the enthalpy of the system decreases (ΔH is negative).

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases (gets cold).** A chemical reaction is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, **the temperature of the surroundings increases.** See Figure 4.2.1.

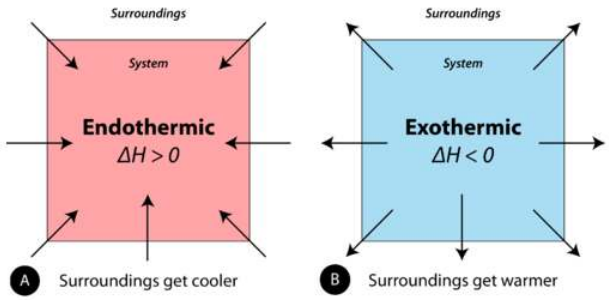
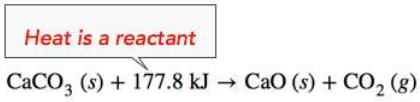


Figure 4.2.1: (A) Endothermic reaction. (B) Exothermic reaction.

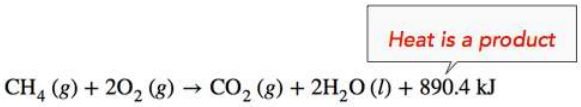
Endothermic reaction: surroundings get cooler and delta H is greater than 0, Exothermic reaction: surroundings get warmer and delta H is less than 0

Endothermic Reaction: When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a **reactant**. The **ΔH is positive** for an endothermic reaction.



$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad \Delta H = +177.8\ kJ$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of **1 mol** of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the **product** side of the reaction. Another way is to write the **heat of reaction** (ΔH) information with a **negative** sign, **−890.4 kJ**.



$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4\ kJ$$

✔ Example 4.2.2

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

? Exercise 4.2.2

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\,(g) + 130$ kcal
b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

Answer

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in **Figure 4.2.2**. In endothermic reactions, the reactants have higher bond energy (stronger bonds) than the products. **Strong bonds have lower potential energy than weak bonds**. Hence, the **energy of the reactants is lower than that of the products**. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure **4.2.2*A***. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the **energy of the products is lower than the energy of the reactants,** hence is energetically downhill, shown in Figure **4.2.2*B***. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few

reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

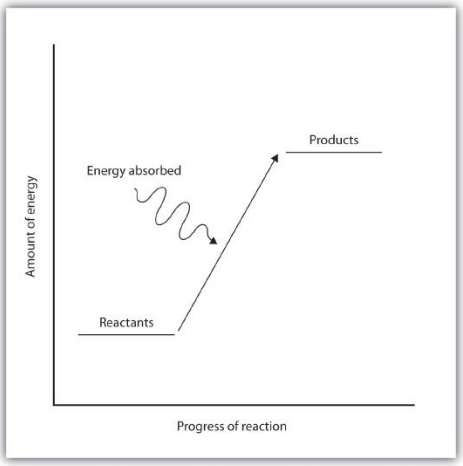


Figure 4.2.2*A*: Endothermic Reactions

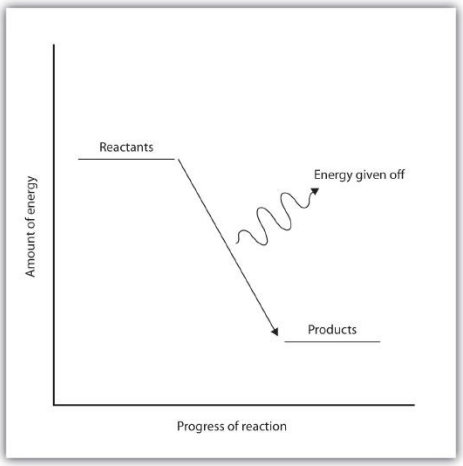


Figure 4.2.2*B*: Exothermic Reactions

Table 4.2.2: Endothermic and Exothermic Reactions

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products	The bonds formed in the products are stronger than the bonds broken in the reactants
The reactants are lower in energy than the products	The products are lower in energy than the reactants
Represented by an "uphill" energy diagram	Represented by an "downhill" energy diagram

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

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4.3: Exothermic and Endothermic Processes

Units of Heat

Heat flow is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by $1°C$. For example, raising the temperature of $100\ g$ of water from $20°C$ to $22°C$ would require $100 \times 2 = 200\ cal$.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains $85\ kcal$ or $85,000\ cal$. In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ kilocalorie = 1\ Calorie = 1000\ calories \tag{4.3.1}$$

To say that the snack "contains" 85 Calories means that $85\ kcal$ of energy are released when that snack is processed by the human body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1\ J = 0.2390\ cal \text{ or } 1\ cal = 4.184\ J \tag{4.3.2}$$

We can calculate the amount of heat released in kilojoules when a 400 Calorie hamburger is digested:

$$400.\ Cal = 400.\ kcal \times \frac{4.184\ kJ}{1\ kcal} = 1.67 \times 10^3\ kJ \tag{4.3.3}$$

Summary

- Common units for heat include Joules (J) and calories (cal); 1 cal = 1.184 J
- 1 food Calorie (Cal) = 1000 cal

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4.4: Heat Capacity and Specific Heat

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends both on its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water under the same sun exposure will not become nearly as hot. This means that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1°C$). Water is very resistant to changes in temperature, while metals generally are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1°C$. The table below lists the specific heats of some common substances. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $(J/g°C)$ or calories per gram per degree $(cal/g°C)$. This text will use $J/g°C$ for specific heat.

Table 4.4.1: Specific Heats of Some Common Substances

Substance	Specific Heat $(J/g°C)$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure **4.4.1**: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake. (CC BY-NC; CK-12)

Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by **1°C**.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by **1°C**.

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4.5: Specific Heat Calculations

Water has a high capacity for absorbing heat. In a car radiator, it serves to keep the engine cooler than it would otherwise run. As the water circulates through the engine, it absorbs heat from the engine block. When it passes through the radiator, the cooling fan and the exposure to the outside environment allow the water to cool somewhat before it makes another passage through the engine.

Specific Heat Calculations

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

Example 4.5.1

A $15.0\ \text{g}$ piece of cadmium metal absorbs $134\ \text{J}$ of heat while rising from 24.0°C to 62.7°C. Calculate the specific heat of cadmium.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Heat $= q = 134\ \text{J}$
- Mass $= m = 15.0\ \text{g}$
- $\Delta T = 62.7^\circ\text{C} - 24.0^\circ\text{C} = 38.7^\circ\text{C}$

Unknown

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^\circ\text{C}} = 0.231\ \text{J/g}^\circ\text{C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known, they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that $60.0\ \text{g}$ of water at 23.52°C was cooled by the removal of $813\ \text{J}$ of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^\circ\text{C} \times 60.0\ \text{g}} = 3.24^\circ\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^\circ\text{C} - 3.24^\circ\text{C} = 20.28^\circ\text{C}$$

Summary

- The specific heat of a substance can be used to calculate the temperature change of the substance when it is heated or cooled.
- Specific heat calculations are illustrated.

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4.6: Enthalpy

The factors influencing a reaction are complicated and varied. Since a catalyst affects activation energy, we might assume it would have some sort of impact on the amount of heat that is absorbed or released by the reaction—but it does not. The change in heat content of a reaction depends solely on the chemical compositions of the reactants and products, not on the path taken to get from one to the other.

Enthalpy

Heat changes in chemical reactions are often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In these cases, the system is at a constant pressure. **Enthalpy** (H) is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds—they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds than that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material being dealt with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Summary

- Enthalpy, the heat content of a system at constant pressure, is related to the heat of reaction.
- The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds.
- Factors that influencing enthalpy include: amount of materials, the state of reactants and products, and direction of the reaction.

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4.7: Calorimetry

At one time, calories in foods were measured with a bomb calorimeter. A weighed amount of the food would be placed in the calorimeter and the system was then sealed and filled with oxygen. An electric spark ignited the food-oxygen mixture. The amount of heat released when the food burned gave an idea of the calories present within the food. Today, calories are calculated from the protein, carbohydrate, and fat content of food (all determined by chemical analysis).

Calorimetry

Calorimetry is the measurement of the transfer of heat into or out of a system during a chemical reaction or physical process. A **calorimeter** is an insulated container that is used to measure heat changes. The majority of reactions that can be analyzed in a calorimetry experiment are either liquids or aqueous solutions. A frequently used and inexpensive calorimeter is a set of nested foam cups fitted with a lid to limit the heat exchange between the liquid in the cup and the air in the surroundings (see figure below). In a typical calorimetry experiment, specific volumes of the reactants are dispensed into separate containers and the temperature of each is measured. They are then mixed into the calorimeter, which starts the reaction. The reactant mixture is stirred until the reaction is complete, while the temperature of the reaction is continuously monitored.

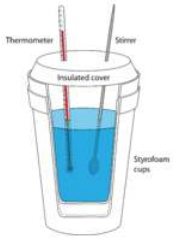


Figure **4.7.1**: A simple constant-pressure calorimeter. (CC BY-NC; CK-12)

The key to all calorimetry experiments is the assumption that there is no heat exchange between the insulated calorimeter and the room. Consider the case of a reaction taking place between aqueous reactants: the water in which the solids have been dissolved is the surroundings, while the dissolved substances are the system. The temperature change that is measured is the temperature change that is occurring in the surroundings. If the temperature of the water increases as the reaction occurs, the reaction is exothermic. Heat was released by the system into the surrounding water. An endothermic reaction absorbs heat from the surroundings, so the temperature of the water decreases as heat leaves the surroundings to enter the system.

The temperature change of the water is measured in the experiment and the specific heat of water can be used to calculate the heat absorbed by the surroundings (q_{surr}).

$$q_{\text{surr}} = m \times c_p \times \Delta T$$

In the equation, m is the mass of the water, c_p is the specific heat of the water, and ΔT is $T_f - T_i$. The heat absorbed by the surroundings is equal, but opposite in sign, to the heat released by the system. Because the heat change is determined at constant pressure, the heat released by the system (q_{sys}) is equal to the enthalpy change (ΔH).

$$q_{\text{sys}} = \Delta H = -q_{\text{surr}} = -(m \times c_p \times \Delta T)$$

The sign of ΔH is positive for an endothermic reaction and negative for an exothermic reaction.

Example **4.7.1**

In an experiment, $25.0\ \text{mL}$ of $1.00\ \text{M HCl}$ at $25.0°\text{C}$ is added to $25.0\ \text{mL}$ of $1.00\ \text{M NaOH}$ at $25.0°\text{C}$ in a foam cup calorimeter. A reaction occurs and the temperature rises to $32.0°\text{C}$. Calculate the enthalpy change (ΔH) in kJ for this reaction. Assume the densities of the solutions are $1.00\ \text{g/mL}$ and that their specific heat is the same as that of water.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $c_p = 4.18\ \text{J/g°C}$

- $V_{\text{final}} = 25.0\ \text{mL} + 25.0\ \text{mL} = 50.0\ \text{mL}$
- $\Delta T = 32.0^\circ\text{C} - 25.0^\circ\text{C} = 7.0^\circ\text{C}$
- Density $= 1.00\ \text{g/mL}$

Unknown

The volume and density can be used to find the mass of the solution after mixing. Then calculate the change in enthalpy by using $\Delta H = q_{\text{sys}} = -q_{\text{surr}} = -(m \times c_p \times \Delta T)$.

Step 2: Solve.

$$m = 50.0\ \text{mL} \times \frac{1.00\ \text{g}}{\text{mL}} = 50.0\ \text{g}$$

$$\Delta H = -(m \times c_p \times \Delta T) = -(50.0\ \text{g} \times 4.18\ \text{J/g}^\circ\text{C} \times 7.0^\circ\text{C}) = -1463\ \text{J} = -1.5\ \text{kJ}$$

Step 3: Think about the result.

The enthalpy change is negative because the reaction releases heat to the surroundings, resulting in an increase in the temperature of the water.

Summary

- Calorimetry is the measurement of the transfer of heat into or out of a system during a chemical reaction or physical process.
- A calorimeter is an insulated container that is used to measure heat changes.
- Calculations involving enthalpy changes are illustrated.

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4.8: Thermochemistry

Heating a home is becoming more and more expensive. The decision to use gas, oil, electricity, or wood can be multi-faceted. Part of the decision is based on which fuel will provide the highest amount of energy release when burned. Studies of thermochemistry can be very useful in getting reliable information for making these important choices.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of $\mathbf{1\ mol}$ of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of a balanced equation:

$$\mathrm{CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + 890.4\,kJ}$$

The equation tells us that $\mathbf{1\ mol}$ of methane combines with $\mathbf{2\ mol}$ of oxygen to produce $\mathbf{1\ mol}$ of carbon dioxide and $\mathbf{2\ mol}$ of water. In the process, $\mathbf{890.4\ kJ}$ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in the figure below.

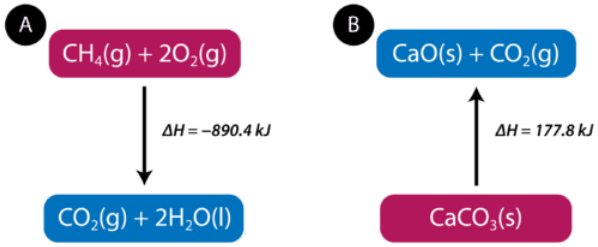


Figure **4.8.1***: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.* (CC BY-NC; CK-12)

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is $\mathbf{-890.4\ kJ}$. The thermochemical reaction can also be written in this way:

$$\mathrm{CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)} \quad \Delta H = -890.4\,\mathrm{kJ}$$

Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation, as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When $\mathbf{1\ mol}$ of calcium carbonate decomposes into $\mathbf{1\ mol}$ of calcium oxide and $\mathbf{1\ mol}$ of carbon dioxide, $\mathbf{177.8\ kJ}$ of heat is absorbed. The process is shown visually in the figure above (B). The thermochemical reaction is shown below.

$$\mathrm{CaCO_3\,(s) + 177.8\,kJ \rightarrow CaO\,(s) + CO_2\,(g)}$$

Because the heat is absorbed by the system, the $\mathbf{177.8\ kJ}$ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)} \quad \Delta H = 177.8\,\mathrm{kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate:

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s) + 177.8\,kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s)} \quad \Delta H = -177.8\,\mathrm{kJ}$$

Summary

- A thermochemical equation is a chemical equation that includes the enthalpy change of the reaction.
- The heat of reaction is the enthalpy change for a chemical reaction.

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4.9: Stoichiometric Calculations and Enthalpy Changes

There is a growing concern about damage to the environment done by emissions from manufacturing plants. Many companies are taking steps to reduce these harmful emissions by adding equipment that will trap the pollutants. In order to know what equipment (and the quantity) to order, studies are done to measure the amount of product currently produced. Since pollution is often both particulate and thermal, energy changes need to be determined in addition to the amounts of products released.

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of $1\ \text{mol}$ of methane released $890.4\ \text{kJ}$, the reaction of $2\ \text{mol}$ of methane would release $2 \times 890.4\ \text{kJ} = 1781\ \text{kJ}$. The reaction of $0.5\ \text{mol}$ of methane would release $\frac{890.4\ \text{kJ}}{2} = 445.2\ \text{kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

Example 4.9.1

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g) + 198\ \text{kJ}$$

Calculate the enthalpy change that occurs when $58.0\ \text{g}$ of sulfur dioxide is reacted with excess oxygen.

Solution:

Step 1: List the known quantities and plan the problem.

- Mass $SO_2 = 58.0\ \text{g}$
- Molar mass $SO_2 = 64.07\ \text{g/mol}$
- $\Delta H = -198\ \text{kJ}$ for the reaction of $2\ \text{mol}\ SO_2$

Unknown

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the moles of SO_2 is multiplied by the conversion factor of $\left(\frac{-198\ \text{kJ}}{2\ \text{mol}\ SO_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0\ \text{g}\ SO_2 \times \frac{1\ \text{mol}\ SO_2}{64.07\ \text{g}\ SO_2} \times \frac{-198\ \text{kJ}}{2\ \text{mol}\ SO_2} = 89.6\ \text{kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than $1\ \text{mol}$. Since $198\ \text{kJ}$ is released for every $2\ \text{mol}$ of SO_2 that reacts, the heat released when about $1\ \text{mol}$ reacts is one half of 198. The $89.6\ \text{kJ}$ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

Summary

- Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems.
- Calculations of energy changes in enthalpy equations are described.

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4.10: Heat of Solution

When preparing dilutions of concentrated sulfuric acid, the directions usually call for adding the acid slowly to water with frequent stirring. When this acid is mixed with water, a great deal of heat is released in the dissolution process. If water were added to acid, the water would quickly heat and splatter, causing harm to the person making the solution.

Heat of Solution

Enthalpy changes also occur when a solute undergoes the physical process of dissolving into a solvent. Hot packs and cold packs (see figure below) use this property. Many hot packs use calcium chloride, which releases heat when it dissolves, according to the equation below.

$$\mathrm{CaCl_2}\,(s) \rightarrow \mathrm{Ca^{2+}}\,(aq) + 2\mathrm{Cl^-}\,(aq) + 82.8\ \mathrm{kJ}$$

The **molar heat of solution** (ΔH_{soln}) of a substance is the heat absorbed or released when one mole of the substance is dissolved in water. For calcium chloride, $\Delta H_{\text{soln}} = -82.8\ \mathrm{kJ/mol}$.



Figure 4.10.1: Chemical hot packs and cold packs work because of the heats of solution of the chemicals inside them. When the bag is squeezed, an inner pouch bursts, allowing the chemical to dissolve in water. Heat is released in the hot pack and absorbed in the cold pack. (CC BY-NC; CK-12)

Many cold packs use ammonium nitrate, which absorbs heat from the surroundings when it dissolves.

$$\mathrm{NH_4NO_3}\,(s) + 25.7\ \mathrm{kJ} \rightarrow \mathrm{NH_4^+}\,(aq) + \mathrm{NO_3^-}\,(aq)$$

Cold packs are typically used to treat muscle strains and sore joints. The cold pack is activated and applied to the affected area. As the ammonium nitrate dissolves, it absorbs heat from the body and helps to limit swelling. For ammonium nitrate, $\Delta H_{\text{soln}} = 25.7\ \mathrm{kJ/mol}$.

Example 4.10.1

The molar heat of solution, ΔH_{soln}, of NaOH is $-44.51\ \mathrm{kJ/mol}$. In a certain experiment, $50.0\ \mathrm{g}$ of NaOH is completely dissolved in $1.000\ \mathrm{L}$ of $20.0^\circ\mathrm{C}$ water in a foam cup calorimeter. Assuming no heat loss, calculate the final temperature of the water.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass $\mathrm{NaOH} = 50.0\ \mathrm{g}$
- Molar mass $\mathrm{NaOH} = 40.00\ \mathrm{g/mol}$
- $\Delta H_{\text{soln}}\ (\mathrm{NaOH}) = -44.51\ \mathrm{kJ/mol}$
- Mass $\mathrm{H_2O} = 1.000\ \mathrm{kg} = 1000.\ \mathrm{g}$ (assumes density $= 1.00\ \mathrm{g/mL}$)
- $T_{\text{initial}}\ (\mathrm{H_2O}) = 20.0^\circ\mathrm{C}$
- $c_p\ (\mathrm{H_2O}) = 4.18\ \mathrm{J/g^\circ C}$

Unknown

This is a multiple-step problem:

1) Grams **NaOH** is converted to moles.

2) Moles is multiplied by the molar heat of solution.

3) The joules of heat released in the dissolution process is used with the specific heat equation and the total mass of the solution to calculate the ΔT.

4) The T_{final} is determined from ΔT.

Step 2: Solve.

$$50.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} \times \frac{-44.51\ \text{kJ}}{1\ \text{mol NaOH}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = -5.56 \times 10^4\ \text{J}$$

$$\Delta T = \frac{\Delta H}{c_p \times m} = \frac{-5.56 \times 10^4\ \text{J}}{4.18\ \text{J/g°C} \times 1050\ \text{g}} = 13.2\text{°C}$$

$$T_{\text{final}} = 20.0\text{°C} + 13.2\text{°C} = 33.2\text{°C}$$

Step 3: Think about your result.

The dissolution process releases a large amount of heat, which causes the temperature of the solution to rise. Care must be taken when preparing concentrated solutions of sodium hydroxide, because of the large amounts of heat released.

Summary

- The molar heat of solution (ΔH_{soln}) of a substance is the heat absorbed or released when one mole of the substance is dissolved in water.
- Sample calculations using molar heat of solution are given.

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4.11: Heat of Combustion

In efforts to reduce gas consumption from oil, ethanol is often added to regular gasoline. It has a high octane rating and burns more slowly than regular gas. This "gasohol" is widely used in many countries. It produces somewhat lower carbon monoxide and carbon dioxide emissions, but does increase air pollution from other materials.

Molar Heat of Combustion

Many chemical reactions are combustion reactions. It is often important to know the energy produced in such a reaction so that we can determine which fuel might be the most efficient for a given purpose. The **molar heat of combustion** (He) is the heat released when one mole of a substance is completely burned.

Typical combustion reactions involve the reaction of a carbon-containing material with oxygen to form carbon dioxide and water as products. If methanol is burned in air, we have:

$$\mathrm{CH_3OH + O_2 \rightarrow CO_2 + 2H_2O} \quad He = 890\ \mathrm{kJ/mol}$$

In this case, one mole of oxygen reacts with one mole of methanol to form one mole of carbon dioxide and two moles of water.

It should be noted that inorganic substances can also undergo a form of combustion reaction:

$$\mathrm{2Mg + O_2 \rightarrow 2MgO}$$

In this case, there is no water and no carbon dioxide formed. For the purposes of this chapter, these reactions are generally not considered in the discussion of combustion reactions.

Example 4.11.1

Heats of combustion are usually determined by burning a known amount of the material in a bomb calorimeter with an excess of oxygen. By measuring the temperature change, the heat of combustion can be determined.

A 1.55 gram sample of ethanol is burned and produced a temperature increase of $\mathrm{55°C}$ in 200 grams of water. Calculate the molar heat of combustion.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass of ethanol $= \mathrm{1.55\ g}$
- Molar mass of ethanol $= \mathrm{46.1\ g/mol}$
- Mass of water $= \mathrm{200\ g}$
- c_p water $= \mathrm{4.18\ J/g^oC}$
- Temperature increase $= \mathrm{55°C}$

Unknown

Step 2: Solve.

Amount of ethanol used:

$$\frac{\mathrm{1.55\ g}}{\mathrm{46.1\ g/mol}} = \mathrm{0.0336\ mol}$$

Energy generated:

$$\mathrm{4.184\ J/g^oC \times 200\ g \times 55°C = 46024\ J = 46.024\ kJ}$$

Molar heat of combustion:

$$\frac{\mathrm{46.024\ kJ}}{\mathrm{0.0336\ mol}} = \mathrm{1370\ kJ/mol}$$

Step 3: Think about your result.

The burning of ethanol produces a significant amount of heat.

Summary

- The molar heat of combustion (He) is the heat released when one mole of a substance is completely burned.
- Calculations using the molar heat of combustion are described.

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4.12: Hess's Law

Learning Objective

- Learn how to combine chemical equations and their enthalpy changes.

Now that we understand that chemical reactions occur with a simultaneous change in energy, we can apply the concept more broadly. To start, remember that some chemical reactions are rather difficult to perform. For example, consider the combustion of carbon to make carbon monoxide:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \Delta H = \?$$

In reality, this is extremely difficult to do. Given the opportunity, carbon will react to make another compound, carbon dioxide:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \Delta H = -393.5 kJ$$

Is there a way around this? Yes. It comes from the understanding that chemical equations can be treated like algebraic equations, with the arrow acting like the equals sign. Like algebraic equations, chemical equations can be combined, and if the same substance appears on both sides of the arrow, it can be canceled out (much like a spectator ion in ionic equations). For example, consider these two reactions:

$$2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) {}_2CO_2(g) \longrightarrow 2\,CO(g) + O_2(g)$$

If we added these two equations by combining all the reactants together and all the products together, we would get

$$2\,C(s) + 2\,O_2(g) + 2\,CO_2(g) \longrightarrow 2\,CO_2(g) + 2\,CO(g) + O_2(g)$$

We note that $2CO_2(g)$ appears on both sides of the arrow, so they cancel:

$$2\,C(s) {}_2^+ O_2(g) {}^+ \cancel{2CO_2(g)} \rightarrow \cancel{2CO_2(g)} + 2\,CO(g) {}^+ O_2(g)$$

We also note that there are 2 mol of O_2 on the reactant side, and 1 mol of O_2 on the product side. We can cancel 1 mol of O_2 from both sides:

$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO(g) {}^+ O_2(g)$$

What do we have left?

$$2\,C(s) + O\ 2(g) \longrightarrow 2\,CO(g)$$

This is the reaction we are looking for! So by algebraically combining chemical equations, we can generate new chemical equations that may not be feasible to perform.

What about the enthalpy changes? **Hess's law** states that when chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way. Two corollaries immediately present themselves:

1. If a chemical reaction is reversed, the sign on ΔH is changed.
2. If a multiple of a chemical reaction is taken, the same multiple of the ΔH is taken as well.

What are the equations being combined? The first chemical equation is the combustion of C, which produces CO_2:

$$2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g)$$

This reaction is two times the reaction to make CO_2 from $C(s)$ and $O_2(g)$, whose enthalpy change is known:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \Delta H = -393.5 kJ$$

According to the first corollary, the first reaction has an energy change of two times −393.5 kJ, or −787.0 kJ:

$$2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) \Delta H = -787.0 kJ$$

The second reaction in the combination is related to the combustion of CO(g):

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) \Delta H = -566.0 kJ$$

The second reaction in our combination is the reverse of the combustion of CO. When we reverse the reaction, we change the sign on the ΔH:

$$2\,CO_2\,(g) \longrightarrow 2\,CO\,(g) + O_2\,(g) \Delta H = +566.0 kJ$$

Now that we have identified the enthalpy changes of the two component chemical equations, we can combine the Δ*H* values and add them:

$$\begin{cases} 2C(s) + 2O_2(g) \rightarrow 2CO_2(g) & \Delta H = -787.0 kJ \\ \cancel{2CO_2(g)} \rightarrow 2CO(g)) + \cancel{O_2(g)} & \Delta H = +566.0 kJ \\ \text{---------------------------} & \\ 2C(s) + O_2(g) \rightarrow 2CO(g) & \Delta H = -787.0 + 566.0 = -221.0 kJ \end{cases}$$

Hess's law is very powerful. It allows us to combine equations to generate new chemical reactions whose enthalpy changes can be calculated, rather than directly measured.

Example 4.12.1:

Determine the enthalpy change of

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O \Delta H = \?$$

from these reactions:

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \Delta H = -174.5 kJ$$

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O \Delta H = -1,692.2 kJ$$

$$2\,CO_2 + H_2 \longrightarrow 2\,O_2 + C_2H_2 \Delta H = -167.5 kJ$$

Solution

We will start by writing chemical reactions that put the correct number of moles of the correct substance on the proper side. For example, our desired reaction has C_2H_4 as a reactant, and only one reaction from our data has C_2H_4. However, it has C_2H_4 as a product. To make it a reactant, we need to reverse the reaction, changing the sign on the Δ*H*:

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \Delta H = +174.5 kJ$$

We need CO_2 and H_2O as products. The second reaction has them on the proper side, so let us include one of these reactions (with the hope that the coefficients will work out when all of our reactions are added):

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O \Delta H = -1,692.2 kJ$$

We note that we now have 4 mol of CO_2 as products; we need to get rid of 2 mol of CO_2. The last reaction has $2CO_2$ as a reactant. Let us use it as written:

$$2\,CO_2 + H_2 \longrightarrow 2\,O_2 + C_2H_2 \Delta H = -167.5 kJ$$

We combine these three reactions, modified as stated:

$$\begin{array}{rl} C_2H_4 \rightarrow C_2H_2 + H_2 & \Delta H = +174.5 \text{ kJ} \\ 2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O & \Delta H = -1{,}692.2 \text{ kJ} \\ 2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2 & \Delta H = -167.5 \text{ kJ} \\ \hline C_2H_4 + 2C_2H_2 + 5O_2 + 2CO_2 + H_2 \rightarrow C_2H_2 + H_2 + 4CO_2 + 2H_2O + 2O_2 + C_2H_2 & \end{array}$$

What cancels? $2C_2H_2$, H_2, $2O_2$, and $2CO_2$. What is left is

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

which is the reaction we are looking for. The Δ*H* of this reaction is the sum of the three Δ*H* values:

$$\Delta H = +174.5 - 1{,}692.2 - 167.5 = -1{,}685.2 \text{ kJ}$$

Exercise 4.12.1

Given the thermochemical equations

$$\mathrm{Pb + Cl_2 \longrightarrow PbCl_2} \Delta H = -223 kJ$$

$$\mathrm{PbCl_2 + Cl_2 \longrightarrow PbCl_4} \Delta H = -87 kJ$$

determine ΔH for

$$\mathrm{2\,PbCl_2 \longrightarrow Pb + PbCl_4}$$

Answer

+136 kJ

Key Takeaway

- Hess's law allows us to combine reactions algebraically and then combine their enthalpy changes the same way.

Exercise 4.12.1

1. Define *Hess's law*.
2. What does Hess's law require us to do to the ΔH of a thermochemical equation if we reverse the equation?
3. If the ΔH for

   $C_2H_4 + H_2 \rightarrow C_2H_6$

   is −65.6 kJ, what is the ΔH for this reaction?

   $C_2H_6 \rightarrow C_2H_4 + H_2$
4. If the ΔH for

   $2Na + Cl_2 \rightarrow 2NaCl$

   is −772 kJ, what is the ΔH for this reaction?

   $2NaCl \rightarrow 2Na + Cl_2$
5. If the ΔH for

   $C_2H_4 + H_2 \rightarrow C_2H_6$

   is −65.6 kJ, what is the ΔH for this reaction?

   $2C_2H_4 + 2H_2 \rightarrow 2C_2H_6$
6. If the ΔH for

   $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

   is −2,650 kJ, what is the ΔH for this reaction?

   $6C_2H_6 + 21O_2 \rightarrow 12CO_2 + 18H_2O$
7. The ΔH for

   $C_2H_4 + H_2O \rightarrow C_2H_5OH$

   is −44 kJ. What is the ΔH for this reaction?

   $2C_2H_5OH \rightarrow 2C_2H_4 + 2H_2O$
8. The ΔH for

   $N_2 + O_2 \rightarrow 2NO$

is 181 kJ. What is the ΔH for this reaction?

$NO \rightarrow 1/2N_2 + 1/2O_2$

9. Determine the ΔH for the reaction

$Cu + Cl_2 \rightarrow CuCl_2$

given these data:

$2Cu + Cl_2 \rightarrow 2CuCl \; \Delta H = -274 \text{ kJ} 2CuCl + Cl_2 \rightarrow 2CuCl_2 \; \Delta H = -166 \text{ kJ}$

10. Determine ΔH for the reaction

$2CH_4 \rightarrow 2H_2 + C_2H_4$

given these data:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \; \Delta H = -891 \text{ kJ} C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \; \Delta H = -1{,}411 \text{ kJ} 2H_2 + O_2 \rightarrow 2H_2O \; \Delta H = -571$ kJ

11. Determine ΔH for the reaction

$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$

given these data:

$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \; \Delta H = -1{,}650 \text{ kJ} 2S + 3O_2 \rightarrow 2SO_3 \; \Delta H = -792 \text{ kJ} 2Fe + 3S + 6O_2 \rightarrow Fe_2(SO_4)_3 \; \Delta H = -2{,}583 \text{ kJ}$

12. Determine ΔH for the reaction

$CaCO_3 \rightarrow CaO + CO_2$

given these data:

$2Ca + 2C + 3O_2 \rightarrow 2CaCO_3 \; \Delta H = -2{,}414 \text{ kJ} C + O_2 \rightarrow CO_2 \; \Delta H = -393.5 \text{ kJ} 2Ca + O_2 \rightarrow 2CaO \; \Delta H = -1{,}270 \text{ kJ}$

Answers

1. If chemical equations are combined, their energy changes are also combined.
2.
3. $\Delta H = 65.6$ kJ
4.
5. $\Delta H = -131.2$ kJ
6.
7. $\Delta H = 88$ kJ
8.
9. $\Delta H = -220$ kJ
10.
11. $\Delta H = 570$ kJ

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4.13: Standard Heat of Formation

The Hope diamond, a form of carbon, is a very expensive piece of jewelry—currently worth about $350,000,000. A graphite pencil, comprised partly of carbon, can be purchased for less than a dollar. Both items contain carbon, but there is a big difference in how that carbon is organized. The diamond was formed under very different reaction conditions than the graphite, so it has a different heat of formation.

Standard Heat of Formation

A relatively straightforward chemical reaction is one in which elements are combined to form a compound. Sodium and chlorine react to form sodium chloride. Hydrogen and oxygen combine to form water. Like other reactions, these are accompanied by either the absorption or release of heat. The **standard heat of formation** (ΔH_f°) is the enthalpy change associated with the formation of one mole of a compound from its elements in their standard states. The standard conditions for thermochemistry are $\mathbf{25°C}$ and $\mathbf{101.3\ kPa}$. Therefore, the standard state of an element is its state at $\mathbf{25°C}$ and $\mathbf{101.3\ kPa}$. For example, iron is a solid, bromine is a liquid, and oxygen is a gas under those conditions. The standard heat of formation of an element in its standard state by definition is equal to zero. The $\Delta H_f^\circ = 0$ for the diatomic elements, $H_2\,(g)$, $N_2\,(g)$, $O_2\,(g)$, $F_2\,(g)$, $Cl_2\,(g)$, $Br_2\,(g)$, and $I_2\,(g)$. The graphite form of solid carbon is in its standard state with $\Delta H_f^\circ = 0$, while diamond is not its standard state. Some standard heats of formation are listed in the table below.

Standard Heats of Formation of Selected Substances

Table 4.13.1: Standard Heats of Formation of Selected Substances

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Al_2O_3\,(s)$	-1669.8	$H_2O_2\,(l)$	-187.6
$BaCl_2\,(s)$	-860.1	$KCl\,(s)$	-435.87
$Br_2\,(g)$	30.91	$NH_3\,(g)$	-46.3
$C\,(s, graphite)$	0	$NO\,(g)$	90.4
$C\,(s, diamond)$	1.90	$NO_2\,(g)$	33.85
$CH_4\,(g)$	-74.85	$NaCl\,(s)$	-411.0
$C_2H_5OH\,(l)$	-276.98	$O_3\,(g)$	142.2
$CO\,(g)$	-110.5	$P\,(s, white)$	0
$CO_2\,(g)$	-393.5	$P\,(s, red)$	-18.4
$CaO\,(s)$	-635.6	$PbO\,(s)$	-217.86
$CaCO_3\,(s)$	-1206.9	$S\,(rhombic)$	0
$HCl\,(g)$	-92.3	$S\,(monoclinic)$	0.30
$CuO\,(s)$	-155.2	$SO_2\,(g)$	-296.1
$CuSO_4\,(s)$	-769.86	$SO_3\,(g)$	-395.2
$Fe_2O_3\,(s)$	-822.2	$H_2S\,(s)$	-20.15
$H_2O\,(g)$	-241.8	$SiO_2\,(s)$	-859.3
$H_2O\,(l)$	-285.8	$ZnCl_2\,(s)$	-415.89

Summary

- The standard heat of formation (ΔH_f°) is the enthalpy change associated with the formation of one mole of a compound from its elements in their standard states.
- The standard conditions for thermochemistry are $\mathbf{25°C}$ and $\mathbf{101.3\ kPa}$.

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4.14: Calculating Heat of Reaction from Heat of Formation

Natural diamonds are mined from sites around the world. However, the price of natural diamonds is carefully controlled, so other sources of diamonds are being explored. Several different methods for producing synthetic diamonds are available, usually involving treating carbon at very high temperatures and pressures. The diamonds produced are now of high quality, but are primarily used in industrial applications. Diamonds are one of the hardest materials available and are widely used for cutting and grinding tools.

Calculating Heat of Reaction from Heat of Formation

An application of Hess's law allows us to use standard heats of formation to indirectly calculate the heat of reaction for any reaction that occurs at standard conditions. An enthalpy change that occurs specifically under standard conditions is called the **standard enthalpy (or heat) of reaction** and is given the symbol $\Delta H°$. The standard heat of reaction can be calculated by using the following equation.

$$\Delta H° = \sum n\Delta H_f^\circ \text{ (products)} - \sum n\Delta H_f^\circ \text{ (reactants)}$$

The symbol Σ is the Greek letter sigma and means "the sum of". The standard heat of reaction is equal to the sum of all the standard heats of formation of the products minus the sum of all the standard heats of formation of the reactants. The symbol "n" signifies that each heat of formation must first be multiplied by its coefficient in the balanced equation.

Standard Heats of Formation of Selected Substances

Table 4.14.1: Standard Heats of Formation of Selected Substances

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Al_2O_3\,(s)$	-1669.8	$H_2O_2\,(l)$	-187.6
$BaCl_2\,(s)$	-860.1	$KCl\,(s)$	-435.87
$Br_2\,(g)$	30.91	$NH_3\,(g)$	-46.3
$C\,(s, graphite)$	0	$NO\,(g)$	90.4
$C\,(s, diamond)$	1.90	$NO_2\,(g)$	33.85
$CH_4\,(g)$	-74.85	$NaCl\,(s)$	-411.0
$C_2H_5OH\,(l)$	-276.98	$O_3\,(g)$	142.2
$CO\,(g)$	-110.5	$P\,(s, white)$	0
$CO_2\,(g)$	-393.5	$P\,(s, red)$	-18.4
$CaO\,(s)$	-635.6	$PbO\,(s)$	-217.86
$CaCO_3\,(s)$	-1206.9	$S\,(rhombic)$	0
$HCl\,(g)$	-92.3	$S\,(monoclinic)$	0.30
$CuO\,(s)$	-155.2	$SO_2\,(g)$	-296.1
$CuSO_4\,(s)$	-769.86	$SO_3\,(g)$	-395.2
$Fe_2O_3\,(s)$	-822.2	$H_2S\,(s)$	-20.15
$H_2O\,(g)$	-241.8	$SiO_2\,(s)$	-859.3
$H_2O\,(l)$	-285.8	$ZnCl_2\,(s)$	-415.89

Example 4.14.1

Calculate the standard heat of reaction ($\Delta H°$) for the reaction of nitrogen monoxide gas with oxygen to form nitrogen dioxide gas.

Solution

Step 1: List the known quantities and plan the problem.

Known

- ΔH_f° for $NO\,(g) = 90.4\ kJ/mol$
- ΔH_f° for $O_2\,(g) = 0$ (element)
- ΔH_f° for $NO_2\,(g) = 33.85\ kJ/mol$

Unknown

First write the balanced equation for the reaction. Then apply the equation to calculate the standard heat of reaction from the standard heats of formation.

Step 2: Solve.

The balanced equation is: $2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$

Applying the equation from the text:

$$\begin{aligned}\Delta H° &= [2\ mol\ NO_2\,(33.85\ kJ/mol)] - [2\ mol\ NO\,(90.4\ kJ/mol) + 1\ mol\ O_2\,(0\ kJ/mol)] \\ &= -113\ kJ\end{aligned}$$

The standard heat of reaction is \(-113 \: \text{kJ}\nonumber \]

Step 3: Think about your result.

The reaction is exothermic, which makes sense because it is a combustion reaction and combustion reactions always release heat.

Summary

- An enthalpy change that occurs specifically under standard conditions is called the standard enthalpy (or heat) of reaction and is given the symbol $\Delta H°$.
- Standard heats of reaction can be calculated from standard heats of formation.

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4.15: Thermodynamics- Entropy

When the pieces of a jigsaw puzzle are dumped from the box, the pieces naturally hit the table in a very random pattern. In order to put the puzzle together, a great deal of work must be done to overcome the natural disorder of the pieces. The pieces need to be turned right-side up, then sorted by color or edge (some people like to put the border together first). Finally comes the challenge of finding the exact spot of each piece of the puzzle, in order to obtain the finished picture.

Entropy

There is a tendency in nature for systems to proceed toward a state of greater disorder or randomness. **Entropy** is a measure of the degree of randomness or disorder of a system. Entropy is an easy concept to understand when thinking about everyday situations. The entropy of a room that has been recently cleaned and organized is low. As time goes by, it likely will become more disordered and thus its entropy will increase (see figure below). The natural tendency of a system is for its entropy to increase.

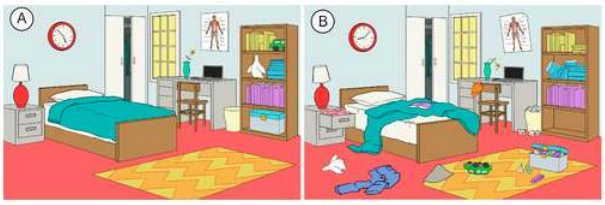


Figure 4.15.1: The messy room on the right has more entropy than the highly ordered room on the left.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system. How can you tell if a certain reaction shows an increase or a decrease in entropy? The molecular state of the reactants and products provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
2. Entropy increases when a substance is broken up into multiple parts. The process of dissolution increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster-moving particles have more disorder than particles that are moving slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when a gas is produced from nongaseous reactants.

These examples serve to illustrate how the entropy change in a reaction can be predicted:

$\mathrm{Cl_2}\,(g) \rightarrow \mathrm{Cl_2}\,(l)$

The entropy is decreasing because a gas is becoming a liquid.

$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g)$

The entropy is increasing because a gas is being produced and the number of molecules is increasing.

$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g)$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s)$

The entropy is decreasing because a solid is formed from aqueous reactants.

$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightarrow 2\mathrm{HCl}\,(g)$

The entropy change is unknown (but likely not zero), because there are equal numbers of molecules on both sides of the equation, and all are gases.

Summary

- Entropy is defined.
- Situations involving entropy changes are described.

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4.16: Standard Entropy

As scientists explore energy supplies, geothermal sources look very appealing. The natural geysers that exist in some parts of the world could possibly be harnessed to provide power for many purposes. The change in energy content and the release of energy caused by steam condensing to liquid can help fill some of our growing energy needs.

Standard Entropy

All molecular motion ceases at absolute zero ($0\,\text{K}$). Therefore, the entropy of a pure crystalline substance at absolute zero is defined to be equal to zero. As the temperature of the substance increases, its entropy increases because of an increase in molecular motion. The absolute or **standard entropy** of substances can be measured. The symbol for entropy is S and the standard entropy of a substance is given by the symbol $S°$, indicating that the standard entropy is determined under standard conditions. The units for entropy are $\text{J/K} \cdot \text{mol}$. Standard entropies for a few substances are shown in the table below.

Standard Entropy Values at **25°C**

Table 4.16.1: Standard Entropy Values at 25°C

Substance	$S°\,(\text{J/K} \cdot \text{mol})$
$\text{H}_2\,(g)$	131.0
$\text{O}_2\,(g)$	205.0
$\text{H}_2\text{O}\,(l)$	69.9
$\text{H}_2\text{O}\,(g)$	188.7
C (graphite)	5.69
C (diamond)	2.4

The knowledge of the absolute entropies of substances allows us to calculate the entropy change ($\Delta S°$) for a reaction. For example, the entropy change for the vaporization of water can be found as follows:

$$\begin{aligned}\Delta S° &= S°\,(\text{H}_2\text{O}\,(g)) - S°\,(\text{H}_2\text{O}\,(l)) \\ &= 188.7\,\text{J/K} \cdot \text{mol} - 69.9\,\text{J/K} \cdot \text{mol} = 118.8\,\text{J/K} \cdot \text{mol}\end{aligned}$$

The entropy change for the vaporization of water is positive because the gas state has higher entropy than the liquid state.

In general, the entropy change for a reaction can be determined if the standard entropies of each substance are known. The equation below can be applied.

$$\Delta S° = \Sigma n S°\ (\text{products}) - \Sigma n S°\ (\text{reactants})$$

The standard entropy change is equal to the sum of the standard entropies of the products minus the sum of the standard entropies of the reactants. The symbol "n" signifies that each entropy must first be multiplied by its coefficient in the balanced equation. The entropy change for the formation of liquid water from gaseous hydrogen and oxygen can be calculated using this equation:

$$\begin{aligned}&2\text{H}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{H}_2\text{O}\,(l) \\ &\Delta S° = 2\,(69.9) - [2\,(131.0) + 1\,(205.0)] = -327\,\text{J/K} \cdot \text{mol}\end{aligned}$$

The entropy change for this reaction is highly negative because three gaseous molecules are being converted into two liquid molecules. According to the drive towards higher entropy, the formation of water from hydrogen and oxygen is an unfavorable reaction. In this case, the reaction is highly exothermic, and the drive towards a decrease in energy allows the reaction to occur.

Summary

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4.17: Entropy Changes in Chemical Reactions

Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at °0C at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

$$\mathrm{H_2O\,(s)} \rightarrow \mathrm{H_2O\,(l)} \tag{4.17.1}$$

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

> *However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)*

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

Standard Molar Entropy, S^0

The entropy of a substance has an absolute value of 0 entropy at 0 K.

- **Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in Table T2.
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the *n*, and *m*, terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^0 = \sum_n nS^0(products) - \sum_m mS^0(reactants)$$

Example 4.17.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

At 298K as a standard temperature:

- $S^0(NH_3)$ = 192.5 J/mol K
- $S^0(H_2)$ = 130.6 J/mol K
- $S^0(N_2)$ = 191.5 J/mol K

Solution

From the balanced equation we can write the equation for ΔS^0 (the change in the standard molar entropy for the reaction):

$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$

$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$

$\Delta S^0 = -198.3$ J/mol K

It would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the $N_2(g)$ used to float around independently of the H_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example **4.17.2** illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

Example 4.17.2: Combustion of Octane

Use the data in Table T2 to calculate ΔS° for the combustion reaction of liquid isooctane with O_2(g) to give CO_2(g) and H_2O(g) at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table T2. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$\mathrm{C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(g)}$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ &= [8S^\circ(\mathrm{CO_2}) + 9S^\circ(\mathrm{H_2O})] - [S^\circ(\mathrm{C_8H_{18}}) + \frac{25}{2}S^\circ(\mathrm{O_2})]\\ &= \{[8\text{ mol }\mathrm{CO_2} \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol }\mathrm{H_2O} \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol }\mathrm{C_8H_{18}} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise 4.17.2

Use the data in Table T2 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer

−361.1 J/K



Calculating the Entropy of Reaction using S: Calculating the Entropy of Reaction using S(opens in new window) [youtu.be]

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4.18: Spontaneous and Nonspontaneous Reactions

Nitroglycerin is a tricky substance. An active ingredient in dynamite (where it is stabilized), "raw" nitroglycerin is very unstable. Physical shock will cause the material to explode. The reaction is shown below.

$$4_3CH_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

The explosion of nitroglycerin releases large volumes of gases and is very exothermic.

Spontaneous Reactions

Reactions are favorable when they result in a decrease in enthalpy and an increase in entropy of the system. When both of these conditions are met, the reaction occurs naturally. A **spontaneous reaction** is a reaction that favors the formation of products at the conditions under which the reaction is occurring. A roaring bonfire is an example of a spontaneous reaction, since it is exothermic (there is a decrease in the energy of the system as energy is released to the surroundings as heat). The products of a fire are composed partly of gases such as carbon dioxide and water vapor. The entropy of the system increases during a combustion reaction. The combination of energy decrease and entropy increase dictates that combustion reactions are spontaneous reactions.



Figure **4.18.1**: Bonfire.

A **nonspontaneous reaction** is a reaction that does not favor the formation of products at the given set of conditions. In order for a reaction to be nonspontaneous, it must be endothermic, accompanied by a decrease in entropy, or both. Our atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide:

$$N_2\,(g) + O_2\,(g) \rightarrow 2NO\,(g)$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures. It is a highly endothermic reaction with a slightly positive entropy change (ΔS). Nitrogen monoxide is capable of being produced at very high temperatures and has been observed to form as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. A piece of paper will not suddenly burst into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

In a reversible reaction, one reaction direction may be favored over the other. Carbonic acid is present in carbonated beverages. It decomposes spontaneously to carbon dioxide and water, according to the following reaction.

$$H_2CO_3\,(aq) \rightleftharpoons CO_2\,(g) + H_2O\,(l)$$

If you were to start with pure carbonic acid in water and allow the system to come to equilibrium, more than 99% of the carbonic acid would be converted into carbon dioxide and water. The forward reaction is spontaneous because the products of the forward

reaction are favored at equilibrium. In the reverse reaction, carbon dioxide and water are the reactants, and carbonic acid is the product. When carbon dioxide is bubbled into water, less than 1% is converted to carbonic acid when the reaction reaches equilibrium. The reverse reaction, as written above, is not spontaneous.

Summary

- Spontaneous and nonspontaneous reactions are defined.
- Examples of both types of reactions are given.

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4.19: Thermodynamics- Free Energy

The steam engine pictured below is slowly going out of style, but is still a picturesque part of the modern railroad. The water in a boiler is heated by a fire (usually fueled by coal) and turned to steam. This steam then pushes the pistons that drive the wheels of the train. It is the pressure created by the steam which allows work to be done in moving the train.



Figure **4.19.1**: A steam locomotive.

Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** is energy that is available to do work. Spontaneous reactions release free energy as they proceed. Recall that the determining factors for spontaneity of a reaction are the enthalpy and entropy changes that occur for the system. The free energy change of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{4.19.1}$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states. The usual units for ΔH is $\mathrm{kJ/mol}$, while ΔS is often reported in $\mathrm{J/K \cdot mol}$. It is necessary to change the units for ΔS to $\mathrm{kJ/K \cdot mol}$, so that the calculation of ΔG is in $\mathrm{kJ/mol}$.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. The reaction that has a negative ΔG is called **exergonic**.A nonspontaneous reaction is one that requires free energy, and so the sign of ΔG is positive. The reaction that has a positive ΔG is called **endergonic**. Since ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different general outcomes for ΔG and these are outlined in the table below.

Table 4.19.1: Enthalpy, Entropy, and Free Energy Changes

ΔH	ΔS	ΔG
- value (exothermic)	+ value (disordering)	always negative (spontaneous, exergonic)
+ value (endothermic)	+ value (disordering)	negative at higher temperatures
- value (exothermic)	- value (ordering)	negative at lower temperatures
+ value (endothermic)	- value (ordering)	always positive (nonspontaneous, endergonic)

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature and so can only be positive. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of

ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T\Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice. At a relatively low temperature (below $273\ \text{K}$), the melting is not spontaneous because the positive ΔH term "outweighs" the $T\Delta S$ term. When the temperature rises above $273\ \text{K}$, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term that favors the reaction. In this case, a spontaneous reaction is dependent upon the $T\Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273\ \text{K}$, the larger $T\Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Summary

- Free energy is defined.
- Relationships between enthalpy, entropy, and free energy are described.

Contributors and Attributions

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4.20: Calculating Free Energy Change (Δ G o)

When you are baking something, you heat the oven to the temperature indicated in the recipe. Then you mix all the ingredients, put them in the proper baking dish, and place them in the oven for a specified amount of time. If you had mixed the ingredients and left them out at room temperature, not much would change. The materials need to be heated to a given temperature, for a set time, in order for the ingredients to react with one another and produce a delicious final product.

Calculating Free Energy (ΔG^o)

The free energy change of a reaction can be calculated using the following expression:

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

where ΔG = free energy change $(\mathrm{kJ/mol})$

ΔH = change in enthalpy $(\mathrm{kJ/mol})$

ΔS = change in entropy $(\mathrm{J/K \cdot mol})$

T = temperature (Kelvin)

Note that all values are for substances in their standard state. In performing calculations, it is necessary to change the units for ΔS to $\mathrm{kJ/K \cdot mol}$, so that the calculation of ΔG is in $\mathrm{kJ/mol}$.

Example 4.20.1

Methane gas reacts with water vapor to produce a mixture of carbon monoxide and hydrogen, according to the balanced equation below.

$$\mathrm{CH_4}\,(g) + \mathrm{H_2O}\,(g) \rightarrow \mathrm{CO}\,(g) + 3\mathrm{H_2}\,(g)$$

The ΔH^o for the reaction is $+206.1\ \mathrm{kJ/mol}$, while the ΔS^o is $+215\ \mathrm{J/K \cdot mol}$. Calculate the ΔG^o at 25^oC and determine if the reaction is spontaneous at that temperature.

Solution:

Step 1: List the known values and plan the problem.

Known

- $\Delta H^o = 206.1\ \mathrm{kJ/mol}$
- $\Delta S^o = 215\ \mathrm{J/K \cdot mol} = 0.215\ \mathrm{kJ/K \cdot mol}$
- $T = 25^oC = 298\ \mathrm{K}$

Unknown

Prior to substitution into the Gibbs free energy equation, the entropy change is converted to $\mathrm{kJ/K \cdot mol}$ and the temperature to Kelvins.

Step 2: Solve.

$$\Delta G^o = \Delta H^o - T\Delta S^o = 206.1\ \mathrm{kJ/mol} - 298\ \mathrm{K}\,(0.215\ \mathrm{kJ/K \cdot mol}) = +142.0\ \mathrm{kJ/mol}$$

The resulting positive value of ΔG indicates that the reaction is not spontaneous at 25^oC.

Step 3: Think about your result.

The unfavorable driving force of increasing enthalpy outweighed the favorable increase in entropy. The reaction will be spontaneous only at some elevated temperature.

Available values for enthalpy and entropy changes are generally measured at the standard conditions of 25^oC and $1\ \mathrm{atm}$ pressure. The values are slightly temperature dependent and so we must use caution when calculating specific ΔG values at temperatures other than 25^oC. However, since the values for ΔH and ΔS do not change a great deal, the tabulated values can safely be used when making general predictions about the spontaneity of a reaction at various temperatures.

Summary

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4.21: Temperature and Free Energy

Iron ore ($\mathrm{Fe_2O_3}$) and coke (an impure form of carbon) are heated together to make iron and carbon dioxide. The reaction is non-spontaneous at room temperature, but becomes spontaneous at temperatures above $842\ \mathrm{K}$. The iron can then be treated with small amounts of other materials to make a variety of steel products.

Temperature and Free Energy

Consider the reversible reaction in which calcium carbonate decomposes into calcium oxide and carbon dioxide gas. The production of CaO (called quicklime) has been an important reaction for centuries.

$$\mathrm{CaCO_3}\,(s) \rightleftharpoons \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g)$$

The $\Delta H°$ for the reaction is $177.8\ \mathrm{kJ/mol}$, while the $\Delta S°$ is $160.5\ \mathrm{J/K \cdot mol}$. The reaction is endothermic with an increase in entropy due to the production of a gas. We can first calculate the $\Delta G°$ at $25°\mathrm{C}$ in order to determine if the reaction is spontaneous at room temperature.

$$\Delta G° = \Delta H° - T\Delta S° = 177.8\ \mathrm{kJ/mol} - 298\ \mathrm{K}\,(0.1605\ \mathrm{kJ/K \cdot mol}) = 130.0\ \mathrm{kJ/mol}$$

Since the $\Delta G°$ is a large positive quantity, the reaction strongly favors the reactants and very little products would be formed. In order to determine a temperature at which $\Delta G°$ will become negative, we can first solve the equation for the temperature when $\Delta G°$ is equal to zero.

$$0 = \Delta H° - T\Delta S°$$
$$T = \frac{\Delta H°}{\Delta S°} = \frac{177.8\ \mathrm{kJ/mol}}{0.1605\ \mathrm{kJ/K \cdot mol}} = 1108\ \mathrm{K} = 835°\mathrm{C}$$

So at any temperature higher than $835°\mathrm{C}$, the value of $\Delta G°$ will be negative and the decomposition reaction will be spontaneous.



Figure 4.21.1: This lime kiln in Cornwall was used to produce quicklime (calcium oxide), an important ingredient in mortar and cement.

Recall that the assumption that $\Delta H°$ and $\Delta S°$ are independent of temperature means that the temperature at which the sign of $\Delta G°$ switches from being positive to negative ($835°\mathrm{C}$) is an approximation. It is also important to point out that one should not assume that absolutely no products are formed below $835°\mathrm{C}$ and that at that temperature, decomposition suddenly begins. Rather, at lower temperatures, the amount of products formed is simply not great enough to say that the products can be detected by monitoring the pressure of the $\mathrm{CO_2}$ gas that is produced. Above about $700°\mathrm{C}$, measurable amounts of $\mathrm{CO_2}$ are produced. The pressure of $\mathrm{CO_2}$ at equilibrium gradually increases with increasing temperature. Above $835°$, the pressure of $\mathrm{CO_2}$ at equilibrium begins to exceed $1\ \mathrm{atm}$, the standard-state pressure. This is an indication that the products of the reaction are now favored above that temperature. When quicklime is manufactured, the $\mathrm{CO_2}$ is constantly removed from the reaction mixture as it is produced. This causes the reaction to be driven towards the products, according to Le Chatelier's principle.

Summary

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4.22: Changes of State and Free Energy

Energy in a body of water can be gained or lost, dependent on conditions. When water is heated above a certain temperature, steam is generated. The increase in heat energy creates a higher level of disorder in the water molecules as they boil off and leave the liquid.

Changes of State and Free Energy

At the temperature at which a change of state occurs, the two states are in equilibrium with one another. For an ice-water system, equilibrium takes place at $0°C$, so $\Delta G°$ is equal to 0 at that temperature. The heat of fusion of water is known to be equal to $6.01\ \text{kJ/mol}$, and so the Gibbs free energy equation can be solved for the entropy change that occurs during the melting of ice. The symbol ΔS_{fus} represents the entropy change during the melting process, while T_{f} is the freezing point of water.

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{f}}} = \frac{6.01\ \text{kJ/mol}}{273\ \text{K}} = 0.0220\ \text{kJ/K} \cdot \text{mol} = 22.0\ \text{J/K} \cdot \text{mol}$$

The entropy change is positive as the solid state changes into the liquid state. If the transition went from the liquid to the solid state, the numerical value for ΔS would be the same, but the sign would be reversed, since the phase changes indicates going from a less ordered to a more ordered situation.

A similar calculation can be performed for the vaporization of liquid to gas. In this case, we use the molar heat of vaporization. This value is $40.79\ \text{kJ/mol}$. The ΔS_{vap} is as follows:

$$\Delta S = \frac{40.79\ \text{kJ/mol}}{373\ \text{K}} = 0.1094\ \text{kJ/K} \cdot \text{mol} = 109.4\ \text{J/K} \cdot \text{mol}$$

The value is positive, reflecting the increase in disorder going from liquid to vapor. Condensation from vapor to liquid would give a negative value for ΔS.

Summary

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4.23: The Gibbs Free Energy and Cell Voltage

Learning Objectives

- To understand the relationship between cell potential and spontaneous reactions.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that [Ni^{2+}] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \text{J}}{1\ \text{V}} = 1\ \text{C} = \text{A} \cdot \text{s} \tag{4.23.1}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$F = (1.60218 \times 10^{-19}\ \text{C}) \left(\frac{6.02214 \times 10^{23}}{1\ \text{mol e}^-} \right) \tag{4.23.2}$$

$$= 9.64833212 \times 10^4\ \text{C/mol e}^- \simeq 96,485/(\text{V} \cdot \text{mol e}^-) \tag{4.23.3}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell} \tag{4.23.4}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell} \tag{4.23.5}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{4.23.6}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 4.23.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in the standard reduction potentials, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Then use Equation 4.23.6 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From the Standard reduction potential table, we can find the reduction and oxidation half-reactions and corresponding E° values:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.23\ \text{V} \\ \text{anode:} & \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} & E^\circ_{\text{anode}} = 1.09\ \text{V} \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E° is not affected:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.23\ \text{V} \\ \text{anode:} & \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} & E^\circ_{\text{anode}} = 1.09\ \text{V} \\ \text{overall:} & \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} & E^\circ_{\text{cell}} = 0.14\ \text{V} \end{array}$$

B

We can now calculate ΔG° using Equation 4.23.6. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^\circ &= -(n)(F)(E^\circ_{\text{cell}}) \\ &= -(6\ \text{mole})[96,468\ \text{J/(V}\cdot\text{mol)}(0.14\ \text{V})] \\ &= -8.1 \times 10^4\ \text{J} \\ &= -81\ \text{kJ/mol}\ \mathrm{Cr_2O_7^{2-}} \end{aligned}$$

Thus ΔG^o is −81 kJ for the reaction as written, and the reaction is spontaneous.

Summary

The signs of ΔG° and E°_{cell} determine the direction of spontaneous reaction under standard conditions.

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CHAPTER OVERVIEW

5: Reaction Rates

5.1: Concept of Reaction Rate
5.2: Measuring Reaction Rates- Rate Expression
5.3: Collision Theory
5.4: Activation Energy
5.5: Potential Energy Diagrams
5.6: Activated Complex
5.7: Factors Affecting Reaction Rates
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5.8: Rate Laws- predicting reaction rate

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5.1: Concept of Reaction Rate

Drag racing is a sport that involves two cars starting from a dead stop, and driving as fast as they can down a quarter-mile strip. At the end of the strip are timers that determine both elapsed time (how long it took for the cars to cover the quarter mile) and top speed (how fast they were going as they went through the timer chute). Both pieces of data are important. One car may accelerate faster and get ahead that way, while the other car may be slower off the line, but can get up to a higher top speed at the end of the run.

Chemical Reaction Rate

Chemical reactions vary widely in terms of the speed with which they occur. Some reactions occur very quickly. If a lit match is brought in contact with lighter fluid or another flammable liquid, it erupts into flames instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes $\mathbf{11.0\ s}$ to run a $\mathbf{100\ m}$ dash, his rate is given by the distance traveled divided by the time.

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s}$$

The sprinter's average running rate for the race is $\mathbf{9.09\ m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must then be greater than $\mathbf{9.09\ m/s}$ so that, taken over the entire race, the average ends up at $\mathbf{9.09\ m/s}$.



Figure 5.1.1: Runner. (CC BY-NC; CK-12)

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** is the change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a $\mathbf{1.00\ M}$ aqueous solution of substance $\mathbf{A}$ was converted to substance $\mathbf{B}$.

$$\mathrm{A}\,(aq) \rightarrow \mathrm{B}\,(aq)$$

Suppose that after 20.0 seconds, the concentration of $\mathbf{A}$ had dropped from $\mathbf{1.00\ M}$ to $\mathbf{0.72\ M}$ as $\mathbf{A}$ was slowly being converted to $\mathbf{B}$. We can express the rate of this reaction as the change in concentration of $\mathbf{A}$ divided by time.

$$\text{rate} = -\frac{\Delta\,[\mathrm{A}]}{\Delta t} = -\frac{[\mathrm{A}]_{\text{final}} - [\mathrm{A}]_{\text{initial}}}{\Delta t}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of $\mathbf{A}$ is its final concentration minus its initial concentration. Because the concentration of $\mathbf{A}$ is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive and the units are molarity per second or $\mathbf{M/s}$.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.014\ \text{M/s}$$

The molarity of $\mathbf{A}$ decreases by an average rate of $\mathbf{0.014\ M}$ every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second $(\mathbf{M/s})$.

Summary

- Chemists need to be concerned with the rates at which chemical reactions occur.
- The reaction rate indicates how fast the reaction proceeds.

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5.3: Collision Theory

Car damage can be very expensive, especially if the driver who did the damage does not have car insurance. Many people have had the experience of backing up while parallel parking and hearing that "bump". Fortunately, cars are often not going fast enough to do any damage. Every once in a while, though, there is a rearrangement of the body parts of a car when it is hit with sufficient speed; then things need to be fixed.

Collision Theory

The behavior of the atoms, molecules, or ions that comprise the reactants is responsible for the rates of a given chemical reaction. **Collision theory** is a set of principles that states that the reacting particles can form products when they collide with one another, provided those collisions have enough kinetic energy and the correct orientation. Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an **ineffective collision**, while the second collision is called an **effective collision**. In other words, an effective collision requires that reactants collide with the right amount of energy and the right orientation

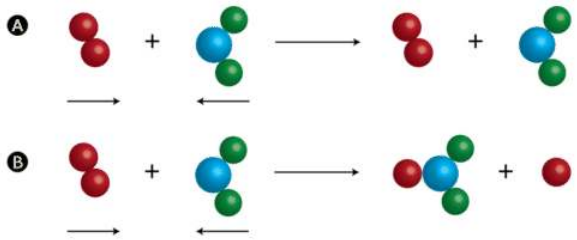


Figure **5.3.1**: An ineffective collision (A) is one that does not result in product formation. An effective collision (B) is one in which chemical bonds are broken and a product is formed. (CC BY-NC; CK-12)

Summary

- Collision theory explains how materials can collide and become new materials.

Contributors and Attributions

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5.4: Activation Energy

The sight of fireworks cascading across the night sky is a hallmark of special occasions. These materials, invented hundreds of years ago, can be dangerous if not handled properly. The chemicals do not react until the fuse burns down and heat is applied to the system. Then, the rocket is launched and explodes high in the sky.

Activation Energy



Figure **5.4.1**: Calcium metal stored in an argon atmosphere. (CC BY-NC; CK-12)

Why do some chemical reactions occur readily while others require input of heat in order to take place? If we mix metallic sodium with water, a reaction occurs immediately, releasing a great deal of heat (enough to ignite the hydrogen gas that is formed). Group II metals, such as calcium, react at a much slower rate. Unlike the extremely vigorous reaction with sodium, the reaction with calcium is slow enough that we can trap the hydrogen gas released.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break, and a chemical reaction more likely to occur, when those particles collide with other particles. The **activation energy** for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction. Some reactions occur readily at room temperature because the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy unless an external source of heat provides the particles with more kinetic energy.

Summary

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5.5: Potential Energy Diagrams

Sisyphus was a mythological being who was a very evil king. As a punishment for his misdoings, he was supposed to roll a large stone up to the top of a long hill. A spell had been placed on the stone so that it would roll back down before reaching the top, never to complete the task. Sisyphus was condemned to an eternity of trying to get to the top of the hill, but never succeeding.

Potential Energy Diagrams

The energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, or sometimes called a reaction progress curve. A **potential energy diagram** shows the change in potential energy of a system as reactants are converted into products. The figure below shows basic potential energy diagrams for an endothermic (A) and an exothermic (B) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

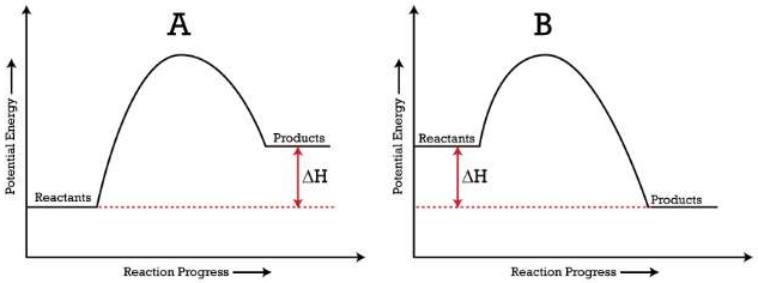


Figure 5.5.1: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (A) In an endothermic reaction, the energy of the products is greater than the energy of the reactants and ΔH is positive. (B) In an exothermic reaction, the energy of the products is lower than the energy of the reactants and ΔH is negative. (CC BY-NC; CK-12)

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome that barrier (see figure below).

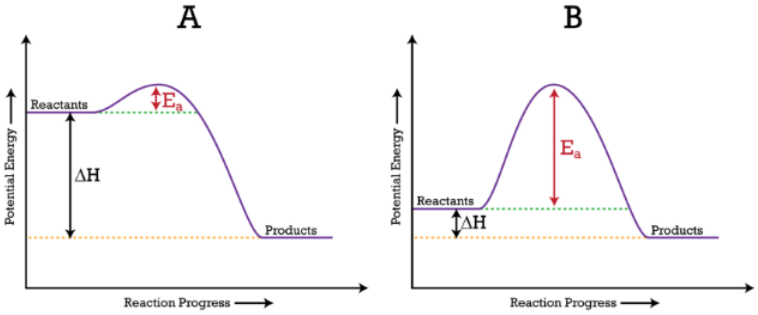


Figure 5.5.2: The activation energy (E_a) of a reaction is the barrier that must be overcome for the reactants to be able to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow. (CC BY-NC; CK-12)

Summary

- A potential energy diagram shows the change in potential energy of a system as reactants are converted into products.
- Potential energy diagrams for endothermic and exothermic reactions are described.
- Diagrams of activation energy and reaction progress are given.

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5.6: Activated Complex

Velcro is a synthetic material that allows fabric (among other things) to stick together. Another more unusual use for Velcro is the sport of "Velcro-jumping". The participant wears clothing made of Velcro and jumps at a Velcro-covered wall. Sometimes the collision with the wall will result in the person sticking to the wall. Other times, the person simply bounces off the wall and does not connect.

Activated Complex

Reactant particles sometimes collide with one another and remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier. Because of its high energy, the activated complex exists for an extremely short period of time (about 10^{-13} s).

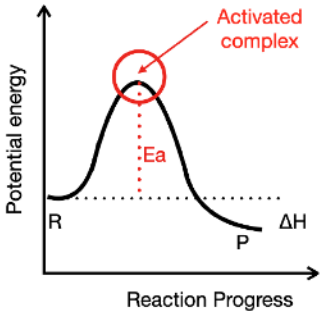


Figure 5.6.1: The activated complex exists momentarily at the peak of the activation energy barrier.

There is an equal likelihood that the activated complex either reforms the original reactants or goes on to form products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules to form water. Because of their unstable nature and brief existence, very little is known about the exact structures of many activated complexes.

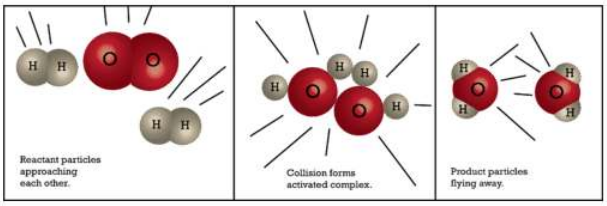


Figure 5.6.2: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve. (CC BY-NC; CK-12)

Summary

- The role of the activated complex in reactions is described.

Contributors and Attributions

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5.7: Factors Affecting Reaction Rates

Learning Objectives

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure **5.7.1**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure **5.7.1**: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area: 2Fe(s) + 6HCl(aq) ⟶ 2FeCl3(aq) + 3H2(g). (surfaceb) An iron nail reacts more slowly.

This figure shows two photos labeled (a) and (b). Photo (a) shows the bottom of a test tube. The test tube is filled with a dark gas, and there is a dark substance and bubbles in the bottom. Photo (b) shows a rod and bubbles in a test tube similar to photo (a), but the gas in the test tube is not as dark.



Video* 5.7.1: The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($\mathbf{CaCO_3}$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **5.7.2**). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathbf{SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)}} \tag{5.7.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathbf{CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}} \tag{5.7.2}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

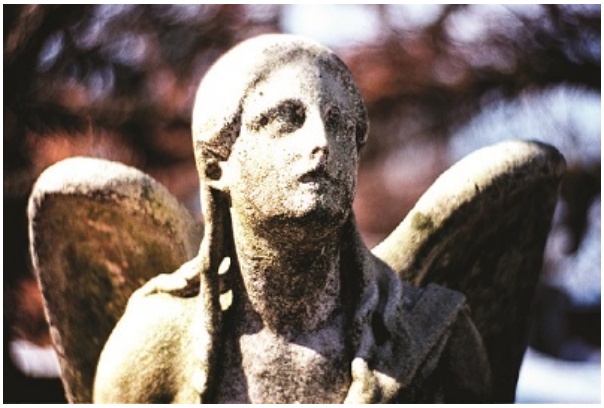


Figure **5.7.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

A photograph is shown of an angel statue. While some details of the statue, including facial features, are present, effects of weathering appear to be diminishing these features.



***Video* 5.7.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure **5.7.3**). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

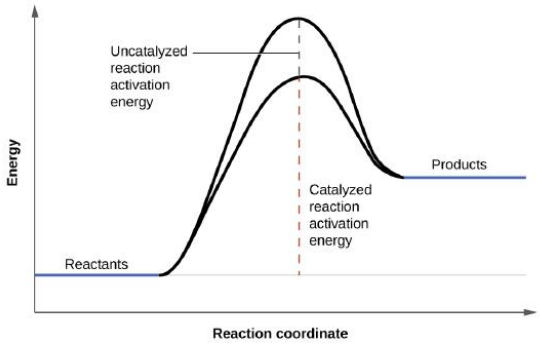


Figure **5.7.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

A graph is shown with the label, "Reaction coordinate," on the x-axis. The x-axis is depicted as an arrow. The y-axis is also an arrow and is labeled, "Energy." There is a horizontal line that runs the width of the graph and appears just above the x-axis. A segment of this line is blue and is labeled, "Reactants." From the right end of this line segment, a solid black, concave down curve is shown which reaches the level just below the end of the y-axis. The curve ends at another short, blue line labeled, "Products." The "Products" line appears at a higher level than the "Reactants" line. An arrow extends from the horizontal line to the apex of the curve. The arrow is labeled, "Uncatalyzed reaction activation energy." A second, black concave down curve is shown. This curve also meets the reactants and products blue line segments, but only extends to about two-thirds the height of the initial curve. From the horizontal line is another arrow pointing to the apex of the second curve. This arrow is labeled, "Catalyzed reaction activation energy."

> *Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.*

Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

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5.7.1: Catalysts

Gasoline-powered vehicles emit various harmful materials. Nitrogen oxides are formed when atmospheric nitrogen reacts with oxygen at the high temperatures found in a car engine. Carbon monoxide is a by-product of the incomplete combustion of hydrocarbons. Evaporated and unused fuel releases volatile hydrocarbons into the atmosphere to help form smog. The presence of a catalytic converter in the exhaust system of the car causes these materials to react and be changed into less harmful products.

Catalysts

Sometimes a particular substance added to a chemical reaction will cause that reaction to undergo a dramatic increase in rate. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and is found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction. After the reaction occurs, a catalyst returns to its original state; so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$\mathrm{H_2O_2\,(aq)} \xrightarrow{\mathrm{MnO_2}} \mathrm{2H_2O\,(l) + O_2\,(g)}$$

A catalyst works by changing the specific way in which the reaction occurs, called its mechanism. The important outcome from the use of a catalyst is that the overall activation energy of the reaction is lowered (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

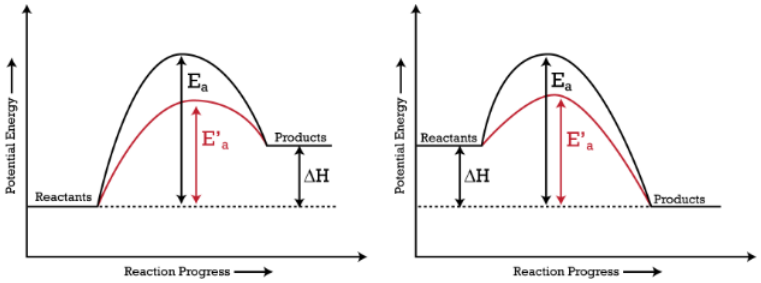


Figure **5.7.1.1**: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E'_a. The heat of reaction (ΔH) is unchanged by the presence of the catalyst. (CC BY-NC; CK-12)

Catalysts are an extremely important part of many chemical reactions. Enzymes in your body acts as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

Summary

- A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction.
- Catalysts are an important part of many chemical reactions.

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5.8: Rate Laws- predicting reaction rate

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. Our discussion so far allow us to **measure** the reaction rate in the lab by measuring the formation of a product or the disappearance of a reactant given certain initial concentrations of reactants, but is there a way to *predict* the reaction rate given the concentration of reactants? The answer is yes.

The **Rate law i**s a mathematical expression that describes the relationship between the rate of a chemical reaction and the concentration of its reactants, and it allows us to **predict the rate of a chemical reaction.** In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p \ldots \tag{5.8.1}$$

in which [*A*], [*B*], and [*C*] represent the molar concentrations of reactants, and *k* is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents *m*, *n*, and *p* are usually positive integers called **reaction orders** (although it is possible for them to be fractions or negative numbers). The **rate constant *k*** and the exponents *m*, *n*, and *p* must be determined *experimentally* by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the concentration of *A*, *B*, or *C*, but it does vary with temperature. **Once the values of *k*, *m*, *n*, and *p* were determined, they can be used to predict the reaction rate for any concentration of *A*, *B*, or *C*.**

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the reaction order. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n \tag{5.8.2}$$

If the exponent *m* is 1, the reaction is first order with respect to *A*, meaning that if the concentration of A doubles, then the reaction rate will also double.

If *m* is 2, the reaction is second order with respect to *A*, meaning that if the concentration of A doubles, then the reaction rate will quadruple.

If *m* is 0, the reaction is zero order in *A*, meaning that the rate of the reaction is not affected by the concentration of that reactant.

The same applies of B. If *n* is 1, the reaction is first order in *B*. If *n* is 2, the reaction is second order in *B*. If *n* is zero, the reaction is zero order in *B*, and the rate of the reaction is not affected by the concentration of that reactant. The **overall reaction order** is the sum of the orders with respect to each reactant. If *m* = 1 and *n* = 1, the overall order of the reaction is second order (*m* + *n* = 1 + 1 = 2).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2] \tag{5.8.3}$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2 \tag{5.8.4}$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-] \tag{5.8.5}$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 5.8.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 5.8.1A

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

Exercise 5.8.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

Determining the reaction orders and the rate constant *k*

It is sometimes helpful to use a more explicit algebraic method, often referred to as the method of initial rates, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Example 5.8.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 5.8.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

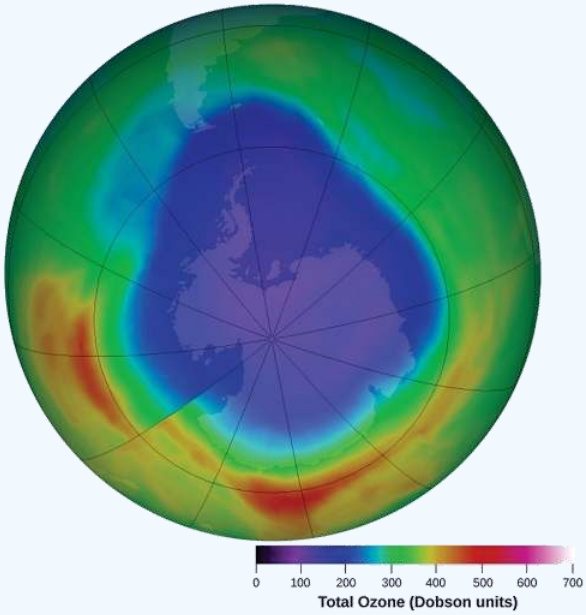


Figure 5.8.1: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

$$\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}$ ($\mathrm{mol\ L^{-1}\ s^{-1}}$)
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}]^n \tag{5.8.6}$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.
2. *Determine the value of* n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3] \tag{5.8.7}$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate*.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \cancel{\text{mol L}^{-1}}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \cancel{\text{mol L}^{-1}})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Exercise 5.8.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g) \tag{5.8.8}$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L^{-1} s^{-1})
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

rate = $k[\text{CH}_3\text{CHO}]^2$ with k = 6.73×10^{-6} L/mol/s

Example 5.8.3: Determining Rate Laws from Reaction Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g) \tag{5.8.9}$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{NO}]}{2\Delta t}$ (mol L^{-1} s^{-1})
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n \tag{5.8.10}$$

As in Example **5.8.2**, we can approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, we will use a different approach to determine the values of *m* and *n*:

Determine the value of m *from the data in which [NO] varies and [Cl_2] is constant.* We can write the ratios with the subscripts *x* and *y* to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n} \tag{5.8.11}$$

Using the third trial and the first trial, in which [Cl_2] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n} \tag{5.8.12}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m} \tag{5.8.13}$$

which simplifies to:

$$2.25 = (1.5)^m \tag{5.8.14}$$

We can use natural logs to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)\frac{\ln(2.25)}{\ln(1.5)} \qquad = m2 = m$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

- *Determine the value of* n *from data in which [Cl_2] varies and [NO] is constant.*

  $$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n} \tag{5.8.15}$$

  Cancelation gives:

  $$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n} \tag{5.8.16}$$

  which simplifies to:

  $$1.5 = (1.5)^n \tag{5.8.17}$$

  Thus *n* must be 1, and the form of the rate law is:

  $$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2] \tag{5.8.18}$$

- *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be mol^{-2} L^2/s so that the rate is in terms of mol/L/s.

  To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

  $$0.00300 \text{ mol L}^{-1} \text{ s}^{-1} = k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1$$
  $$k = 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Exercise 5.8.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\mathrm{OCl^-}(aq) + \mathrm{I^-}(aq) \longrightarrow \mathrm{OI^-}(aq) + \mathrm{Cl^-}(aq) \tag{5.8.19}$$

Trial	[OCl^-] (mol/L)	[I^-] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for *k* yields:

$$\text{rate} = k[\mathrm{OCl^-}]^2[\mathrm{I^-}]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4\ \mathrm{mol^{-2}\ L^2\ s^{-1}}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case. Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\mathrm{NO_2 + CO \longrightarrow NO + CO_2} \quad \text{rate} = k[\mathrm{NO_2}]^2$$

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO} \quad \text{rate} = k[\mathrm{CH_3CHO}]^2$$

$$\mathrm{2\,N_2O_5 \longrightarrow 2\,NO_2 + O_2} \quad \text{rate} = k[\mathrm{N_2O_5}]$$

$$\mathrm{2\,NO_2 + F_2 \longrightarrow 2\,NO_2F} \quad \text{rate} = k[\mathrm{NO_2}][\mathrm{F_2}]$$

$$\mathrm{2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2} \quad \text{rate} = k[\mathrm{NO_2Cl}]$$

> *It is important to note that rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant *k*. In Example 5.8.2, a second-order reaction, we found the units for *k* to be $\mathrm{L\,mol^{-1}\,s^{-1}}$, whereas in Example 5.8.3, a third order reaction, we found the units for *k* to be $\mathrm{mol^{-2}\ L^2/s}$. More generally speaking, the units for the rate constant for a reaction of order $(m + n)$ are $\mathrm{mol^{1-(m+n)}L^{(m+n)-1}s^{-1}}$. Table 5.8.1 summarizes the rate constant units for common reaction orders.

Table **5.8.1**: Rate Constants for Common Reaction Orders

Reaction Order	Units of k
$(m+n)$	$\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$mol^{-2}\ L^2\ s^{-1}$

Note that the units in the table can also be expressed in terms of molarity (*M*) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Contributors and Attributions

Summary

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Glossary

method of initial rates
: use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order
: sum of the reaction orders for each substance represented in the rate law

rate constant (*k*)
: proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law
: (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order
: value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

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CHAPTER OVERVIEW

6: Chemical Equilibrium

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6.1: Reversible Reaction

A solution of cobalt chloride in water is pink due to the presence of the solvated Co^{2+} ion. If sufficient HCl is added, the solution turns blue as the $CoCl_4^{2-}$ ion forms. The reaction can be shifted back to the pink form if more water is added to the solution.



Figure 6.1.1: Cobalt chloride in various stages of equilibrium with hydrochloric acid. (Public Domain; Chemicalinterest via wikipedia)

Chemical Reversibility

Up until this point, we have written the equations for chemical reactions in a way that would seem to indicate that all reactions proceed completely until all the reactants have been converted into products. In reality, a great many chemical reactions do not proceed entirely to completion. A **reversible reaction** is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously. One example of a reversible reaction is the reaction of hydrogen gas and iodine vapor to form hydrogen iodide. The forward and reverse reactions can be written as follows.

$$\text{Forward reaction: } H_2(g) + I_2(g) \rightarrow 2HI(g)$$

$$\text{Reverse reaction: } 2HI(g) \rightarrow H_2(g) + I_2(g)$$

In the forward reaction, hydrogen and iodine combine to form hydrogen iodide. In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. The two reactions can be combined into one equation by the use of a double arrow:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The double arrow is the indication that the reaction is reversible.

When hydrogen and iodine gases are mixed in a sealed container, they begin to react and form hydrogen iodide. At first, only the forward reaction occurs because no HI is present. As the forward reaction proceeds, it begins to slow down as the concentrations of the H_2 and the I_2 decrease. As soon as some HI has formed, it begins to decompose back into H_2 and I_2. The rate of the reverse reaction starts out slow because the concentration of HI is low. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance.

Summary

- A reversible reaction is defined.

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6.2: Chemical Equilibrium

A tug of war involves two teams at the ends of a rope. The goal is to pull the other team over a line in the middle. At first, there is a great deal of tension on the rope, but no apparent movement. A bystander might think that there is nothing happening. In reality, there is a great deal of tension on the rope as the two teams pull in opposite directions at the same time.

Chemical Equilibrium

Hydrogen and iodine gases react to form hydrogen iodide, according to the following reaction:

$$\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$$

$$\textbf{Forward reaction:}\quad \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightarrow 2\mathrm{HI}\,(g)$$

$$\textbf{Reverse reaction:}\quad 2\mathrm{HI}\,(g) \rightarrow \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g)$$

Initially, only the forward reaction occurs because no HI is present. As soon as some HI has formed, it begins to decompose back into $\mathrm{H_2}$ and $\mathrm{I_2}$. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually, the rate of combination of $\mathrm{H_2}$ and $\mathrm{I_2}$ to produce HI becomes equal to the rate of decomposition of HI into $\mathrm{H_2}$ and $\mathrm{I_2}$. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

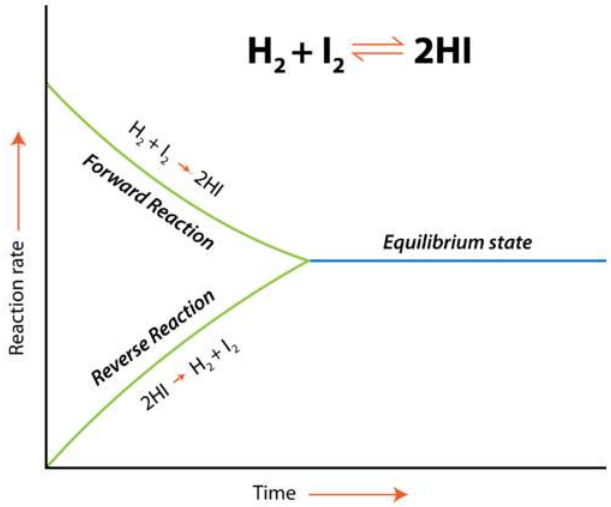


Figure **6.2.1**: Equilibrium in reaction: $\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The figure below shows changes in concentration of $\mathrm{H_2}$, $\mathrm{I_2}$, and HI for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only $\mathrm{H_2}$ and $\mathrm{I_2}$ present. There is no HI initially. As the reaction proceeds toward equilibrium, the concentrations of the $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually decrease, while the concentration of the HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant. In reaction B, the process begins with only HI and no $\mathrm{H_2}$ or $\mathrm{I_2}$. In this case, the concentration of HI gradually decreases while the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

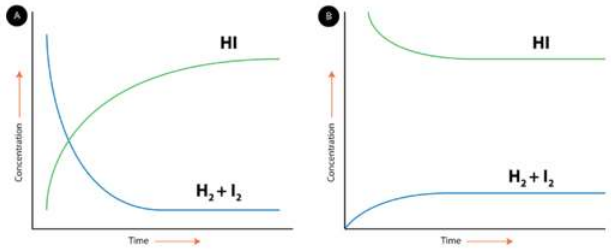


Figure **6.2.2**: Equilibrium between reactants and products.

Conditions for Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both the forward and reverse reactions are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

The description of equilibrium in this concept refers primarily to equilibrium between reactants and products in a chemical reaction. Other types of equilibrium include phase equilibrium and solution equilibrium. A **phase equilibrium** occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A **solution equilibrium** occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.

Summary

- Chemical equilibrium is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.
- Conditions for chemical equilibrium are listed.
- A phase equilibrium occurs when a substance is in equilibrium between two states.
- A solution equilibrium occurs when a solid substance is in a saturated solution.

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6.3: Equilibrium Constant

Consider the hypothetical reversible reaction in which reactants **A** and **B** react to form products **C** and **D**. This equilibrium can be shown below, where the lower case letters represent the coefficients of each substance.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \tag{6.3.1}$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentrations for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}) is the ratio of the mathematical product of the concentrations of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \tag{6.3.2}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units ($\mathrm{mol/L}$).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the previous section, the position of equilibrium for a given reaction does not depend on the starting concentrations and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

It is important to mention that only dissolved substances (aq) or gases (g) appear in the expression of Keq; pure solvents (l) or solids (s) do not. Also We do not use units for equilibrium constants. The convention is to always work with concentrations in molarity (M) and gas pressure in atmospheres (atm) when calculating the K_{eq} values.

Summary

- The equilibrium constant for a reversible reaction is described.

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6.4: Interpreting Equilibrium Constants Values

Learning Objectives

- How to figure out in which direction a reaction will go (i.e. towards making product, or more reactant)
- Calculating equilibrium concentrations. This may involve knowing equilibrium values for some of the reactants and products and determining the concentration of an unknown.
- Alternatively, we may be provided with the starting concentrations of reactants and products and may be asked to find the equilibrium concentrations

Your ability to interpret the numerical value of a quantity in terms of what it means in a practical sense is an essential part of developing a working understanding of Chemistry. This is particularly the case for equilibrium constants, whose values span the entire range of the positive numbers:

- If Keq is a large number (Keq > 1), it means that, at equilibrium, the concentration of the products is large. In this case, the reaction favors the formation of products.
- If Keq is a small number (Keq<1), it means that, at equilibrium, the concentration of the reactants is large. In this case, the reaction favors the formation of reactants.
- If Keq ≈ 1, it means that, at equilibrium, there are significant amounts of both reactants and products.

As an equilibrium constant approaches the limits of infinity, the reaction can be increasingly characterized as a one-way process; we say it is "***complete***" or "***irreversible***".

Kinetically Hindered Reactions

Although it is by no means a general rule, it frequently happens that reactions having very large equilibrium constants are kinetically hindered, often to the extent that the reaction essentially does not take place.

The examples in the following table are intended to show that numbers (values of *Keq*), no matter how dull they may look, do have practical consequences!

Table **6.4.1**: Examples of Reversible Reactions

Reaction	Keq	remarks
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	5×10^{-31} at 25°C, 0.0013 at 2100°C	These two very different values of K illustrate very nicely why reducing combustion-chamber temperatures in automobile engines is environmentally friendly.
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	7×10^{5} at 25°C, 56 at 1300°C	See the discussion of this reaction in the section on the Haber process.
$H_{2(g)} \rightleftharpoons 2H_{(g)}$	10^{-36} at 25°C, 6×10^{-5} at 5000°	Dissociation of any stable molecule into its atoms is endothermic. This means that all molecules will decompose at sufficiently high temperatures.
$H_2O_{(g)} \rightleftharpoons H_{2(g)} + ½O_{2(g)}$	8×10^{-41} at 25°C	You won't find water a very good source of oxygen gas at ordinary temperatures!
$CH_3COOH_{(l)} \rightleftharpoons 2H_2O_{(l)} + 2C_{(s)}$	$K_c = 10^{13}$ at 25°C	This tells us that acetic acid has a great tendency to decompose to carbon, but nobody has ever found graphite (or diamonds!) forming in a bottle of vinegar. A good example of a super kinetically-hindered reaction!

Do Equilibrium Constants have Units?

The equilibrium expression for the synthesis of ammonia

$$3\,H_2\,(g) + N_2\,(g) \longrightarrow 2\,NH_3\,(g) \tag{6.4.1}$$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} \tag{6.4.2}$$

If concentrations are expressed in mol/L, then K_{eq} would be expressed in $mol^{-2}\ L^2$. And yet Keq is often represented as being dimensionless. The reason for this is that, due to the fact that units for the equilibrium depend on the stoichiometric coefficients for each reaction, the Keq units are not consistent. Besides, in carrying out calculations with Keq, the use of units will make things more complicated. Therefore, there is rarely any real need to show the units.

Strictly speaking, we should be consistent in the use of concentrations and always use the same units for reactants and products, that is usually molarity (M) or mol/L.

Summary

The magnitude of the equilibrium constant, Keq, indicates the extent to which a reaction will proceed:

- If Keq is a large number, it means that the equilibrium concentration of the products is large. In this case, the reaction as written will proceed to the right (resulting in an increase in the concentration of products)
- If Keq is a small number, it means that the equilibrium concentration of the reactants is large. In this case, the reaction as written will proceed to the left (resulting in an increase in the concentration of reactants)

Knowing the value of the equilibrium constant, K, will allow us to determine: (1) the direction a reaction will proceed to achieve equilibrium and (2) the ratios of the concentrations of reactants and products when equilibrium is reached

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6.5: Calculations involving Equilibrium Constants and Concentrations at Equilibrium

Iron is an important component of red blood cells. Patients who have low iron will usually be anemic and have a lower than normal number of red blood cells. One way to assess serum iron concentration is with the use of Ferrozine, a complex organic molecule. Ferrozine forms a product with $\mathbf{Fe^{3+}}$, producing a pink color. In order to determine factors affecting the reaction, we need to measure the equilibrium constant. If the equilibrium does not lie far in the direction of products, precautions need to be taken when using this material to measure iron in serum.

Calculating Equilibrium Constants from Concentrations at Equilibrium

The general value of the equilibrium constant gives us information about whether the reactants or the products are favored at equilibrium. Since the product concentrations are in the numerator of the equilibrium expression, a $K_{eq} > 1$ means that the products are favored over the reactants. A $K_{eq} < 1$ means that the reactants are favored over the products.

Though it would often seem that the K_{eq} value would have various units depending on the values of the exponents in the expression, the general rule is that any units are dropped. All K_{eq} values will be reported as having no units.

Example 6.5.1

Equilibrium occurs when nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas:

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g) \tag{6.5.1}$$

At equilibrium at $\mathbf{230°C}$, the concentrations are measured to be $[NO] = 0.0542\ M$, $[O_2] = 0.127\ M$, and $[NO_2] = 15.5\ M$. Calculate the equilibrium constant at this temperature.

Solution:

Step 1: List the known quantities and plan the problem.

Known

- $[NO] = 0.0542\ M$
- $[O_2] = 0.127\ M$
- $[NO_2] = 15.5\ M$

Unknown

- K_{eq} value

The equilibrium expression is first written according to the general form in the text. The equilibrium values are substituted into the expression and the value calculated.

Step 2: Solve.

$$K_{eq} = \frac{[NO_2]^2}{[NO]^2\,[O_2]} \tag{6.5.2}$$

Substituting in the concentrations at equilibrium:

$$K_{eq} = \frac{(15.5)^2}{(0.0542)^2\,(0.127)} = 6.44 \times 10^5 \tag{6.5.3}$$

Step 3: Think about your result.

The equilibrium concentration of the product NO_2 is significantly higher than the concentrations of the reactants NO and O_2. As a result, the K_{eq} value is much larger than 1, an indication that the product is favored at equilibrium.

The equilibrium expression only shows those substances whose concentrations are variable during the reaction. A pure solid or a pure liquid does not have a concentration that will vary during a reaction. Therefore, an equilibrium expression omits pure solids

and liquids, and only shows the concentrations of gases and aqueous solutions. The decomposition of mercury (II) oxide can be shown by the following equation, followed by its equilibrium expression.

$$2\text{HgO}\,(s) \rightleftharpoons 2\text{Hg}\,(l) + \text{O}_2\,(g) \quad K_{\text{eq}} = [\text{O}_2] \tag{6.5.4}$$

The stoichiometry of an equation can also be used in a calculation of an equilibrium constant. At $40°\text{C}$, solid ammonium carbamate decomposes to ammonia and carbon dioxide gases.

$$\text{NH}_4\text{CO}_2\text{NH}_2\,(s) \rightleftharpoons 2\text{NH}_3\,(g) + \text{CO}_2\,(g) \tag{6.5.5}$$

At equilibrium, the $[\text{CO}_2]$ is found to be $4.71 \times 10^{-3}\ \text{M}$. Can the K_{eq} value be calculated from that information alone? Because the ammonium carbamate is a solid, it is not present in the equilibrium expression.

$$K_{\text{eq}} = [\text{NH}_3]^2\,[\text{CO}_2] \tag{6.5.6}$$

The stoichiometry of the chemical equation indicates that as the ammonium carbamate decomposes, $2\ \text{mol}$ of ammonia gas is produced for every $1\ \text{mol}$ of carbon dioxide. Therefore, at equilibrium, the concentration of the ammonia will be twice the concentration of carbon dioxide. So,

$$[\text{NH}_3] = 2 \times \left(4.71 \times 10^{-3}\right) = 9.42 \times 10^{-3}\ \text{M}$$

Substituting these values into the K_{eq} expression:

$$K_{\text{eq}} = \left(9.42 \times 10^{-3}\right)^2 \left(4.71 \times 10^{-3}\right) = 4.18 \times 10^{-7} \tag{6.5.7}$$

Calculating Concentrations at Equilibrium from Equilibrium Constants

The equilibrium constants are known for a great many reactions. Hydrogen and bromine gases combine to form hydrogen bromide gas. At $730°\text{C}$, the equation and K_{eq} are given below.

$$\text{H}_2\,(g) + \text{Br}_2\,(g) \rightleftharpoons 2\text{HBr}\,(g) \quad K_{\text{eq}} = 2.18 \times 10^6 \tag{6.5.8}$$

A certain reaction is begun with only HBr. When the reaction mixture reaches equilibrium at $730°\text{C}$, the concentration of bromine gas is measured to be $0.00243\ \text{M}$. What is the concentration of the H_2 and the HBr at equilibrium?

Since the reaction begins with only HBr and the mole ratio of H_2 to Br_2 is 1:1, the concentration of H_2 at equilibrium is also $0.00243\ \text{M}$. The equilibrium expression can be rearranged to solve for the concentration of HBr at equilibrium:

$$K_{\text{eq}} = \frac{[\text{HBr}]^2}{[\text{H}_2]\,[\text{Br}_2]} \tag{6.5.9}$$

$$[\text{HBr}] = \sqrt{K_{\text{eq}}\,[\text{H}_2]\,[\text{Br}_2]} \tag{6.5.10}$$

$$= \sqrt{2.18 \times 10^6\,(0.00243)\,(0.00243)} = 3.59\ \text{M} \tag{6.5.11}$$

Since the value of the equilibrium constant is very high, the concentration of HBr is much greater than that of H_2 and Br_2 at equilibrium.

Summary

- Calculation of an equilibrium constant is described.

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6.6: Calculations involving Equilibrium Constants and Initial Concentrations

Learning Objective

- Calculate equilibrium concentrations from the values of the initial amounts and the K_{eq}.

There are some circumstances in which, given some initial amounts and the K_{eq}, you will have to determine the concentrations of all species when equilibrium is achieved. Such calculations are not difficult to do, especially if a consistent approach is applied. We will consider such an approach here.

Suppose we have this simple equilibrium. Its associated K_{eq} is 4.0, and the initial concentration of each reactant is 1.0 M:

$$\underset{1.0M}{H_2(g)} + \underset{1.0M}{Cl_2(g)} \rightleftharpoons 2HCl(g) \qquad K_{eq} = 4.0$$

Because we have concentrations for the reactants but not the products, we presume that the reaction will proceed in the forward direction to make products. But by how much will it proceed? We do not know, so let us assign it a variable. Let us assume that x M H_2 reacts as the reaction goes to equilibrium. This means that at equilibrium, we have (1.0 − x) M H_2 left over.

According to the balanced chemical equation, H_2 and Cl_2 react in a 1:1 ratio. How do we know that? The coefficients of these two species in the balanced chemical equation are 1 (unwritten, of course). This means that if x M H_2 reacts, x M Cl_2 reacts as well. If we start with 1.0 M Cl_2 at the beginning and we react x M, we have (1.0 − x) M Cl_2 left at equilibrium.

How much HCl is made? We start with zero, but we also see that 2 mol of HCl are made for every mole of H_2 (or Cl_2) that reacts (from the coefficients in the balanced chemical equation), so if we lose x M H_2, we gain 2x M HCl. So now we know the equilibrium concentrations of our species:

$$\underset{(1.0-x)M}{H_2(g)} + \underset{(1.0-x)M}{Cl_2(g)} \rightleftharpoons \underset{2xM}{2HCl(g)} \qquad K_{eq} = 4.0$$

We can substitute these concentrations into the K_{eq} expression for this reaction and combine it with the known value of K_{eq}:

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

This is an equation in one variable, so we should be able to solve for the unknown value. This expression may look formidable, but first we can simplify the denominator and write it as a perfect square as well:

$$\frac{(2x)^2}{(1-x)^2} = 4.0$$

The fraction is a perfect square, as is the 4.0 on the right. So we can take the square root of both sides:

$$\frac{(2x)}{(1-x)} = 2.0$$

Now we rearrange and solve (be sure you can follow each step):

$$\begin{gathered} 2x = 2.0 - 2.0x \\ 4x = 2.0 \\ x = 0.50 \end{gathered}$$

Now we have to remind ourselves what x is—the amount of H_2 and Cl_2 that reacted—and that 2x is the equilibrium [HCl]. To determine the equilibrium concentrations, we need to go back and evaluate the expressions 1 − x and 2x to get the equilibrium concentrations of our species:

1.0 − x = 1.0 − 0.50 = 0.50 M = [H_2] = [Cl_2]2x = 2(0.50) = 1.0 M = [HCl]

The units are assumed to be molarity. To check, we simply substitute these concentrations and verify that we get the numerical value of the K_{eq}, in this case 4.0:

$$\frac{(1.0)^2}{(0.50)(0.50)} = 4.0$$

We formalize this process by introducing the ICE chart, where ICE stands for initial, change, and equilibrium. The initial values go in the first row of the chart. The change values, usually algebraic expressions because we do not yet know their exact numerical values, go in the next row. However, the change values *must* be in the proper stoichiometric ratio as indicated by the balanced chemical equation. Finally, the equilibrium expressions in the last row are a combination of the initial value and the change value for each species. The expressions in the equilibrium row are substituted into the K_{eq} expression, which yields an algebraic equation that we try to solve.

The ICE chart for the above example would look like this:

	$H_2(g)$	+	$Cl_2(g)$	⇄ ⇄	2HCl(g)	K_{eq} = 4.0
I	1.0		1.0		0	
C	$-x$		$-x$		$+2x$	
E	$1.0 - x$		$1.0 - x$		$+2x$	

Substituting the last row into the expression for the K_{eq} yields

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

which, of course, is the same expression we have already solved and yields the same answers for the equilibrium concentrations. The ICE chart is a more formalized way to do these types of problems. The + sign is included explicitly in the change row of the ICE chart to avoid any confusion.

Sometimes when an ICE chart is set up and the K_{eq} expression is constructed, a more complex algebraic equation will result. One of the more common equations has an x^2 term in it and is called a *quadratic equation*. There will be two values possible for the unknown x, and for a quadratic equation with the general formula $ax^2 + bx + c = 0$ (where a, b, and c are the *coefficients* of the quadratic equation), the two possible values are as follows:

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

One value of x is the + sign used in the numerator, and the other value of x is the − sign used in the numerator. In this case, one value of x typically makes no sense as an answer and can be discarded as physically impossible, leaving only one possible value and the resulting set of concentrations. Example 9 illustrates this.

Example 6.6.1:

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\underset{0.55M}{COI_2(g)} \rightleftharpoons \underset{0}{CO(g)} + \underset{0}{I_2(g)} \qquad K_{eq} = 0.00088$$

Solution

The ICE chart is set up like this. First, the initial values:

	$COI_2(g)$	⇄ ⇄	CO(g)	+	$I_2(g)$
I	0.55		0		0
C					
E					

Some of the COI_2 will be lost, but how much? We do not know, so we represent it by the variable x. So x M COI_2 will be lost, and for each COI_2 that is lost, x M CO and x M I_2 will be produced. These expressions go into the change row:

	$COI_2(g)$	⇄ ⇄	$CO(g)$	+	$I_2(g)$
I	0.55		0		0
C	$-x$		$+x$		$+x$
E					

At equilibrium, the resulting concentrations will be a combination of the initial amount and the changes:

	$COI_2(g)$	⇄ ⇄	$CO(g)$	+	$I_2(g)$
I	0.55		0		0
C	$-x$		$+x$		$+x$
E	$0.55 - x$		$+x$		$+x$

The expressions in the equilibrium row go into the K_{eq} expression:

$$K_{eq} = \frac{[CO][I_2]}{[COI_2]} = 0.00088 = \frac{(x)(x)}{(0.55 - x))}$$

We rearrange this into a quadratic equation that equals 0:

$0.000484 - 0.00088x = x^2x^2 + 0.00088x - 0.000484 = 0$

Now we use the quadratic equation to solve for the two possible values of x:

$$x = \frac{-0.00088 \pm \sqrt{(0.00088)^2 - 4(1)(-0.000484)}}{2(1)}$$

Evaluate for both signs in the numerator—first the + sign and then the − sign:

$x = 0.0216$ or $x = -0.0224$

Because x is the final concentration of both CO and I_2, it cannot be negative, so we discount the second numerical answer as impossible. Thus $x = 0.0216$.

Going back to determine the final concentrations using the expressions in the E row of our ICE chart, we have

$[COI_2] = 0.55 - x = 0.55 - 0.0216 = 0.53$ M$[CO] = x = 0.0216$ M$[I_2] = x = 0.0216$ M

You can verify that these numbers are correct by substituting them into the K_{eq} expression and evaluating and comparing to the known K_{eq} value.

? Exercise 6.6.1

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\underset{0.075M}{N_2H_2(g)} \rightleftharpoons \underset{0}{N_2(g)} + \underset{0}{H_2(g)} \quad K_{eq} = 0.052$$

Answer

The completed ICE chart is as follows:

	$N_2H_2(g)$	⇄ ⇄	$N_2(g)$	+	$H_2(g)$
I	0.075		0		0
C	$-x$		$+x$		$+x$
E	$0.075 - x$		$+x$		$+x$

Solving for x gives the equilibrium concentrations as $[N_2H_2] = 0.033$ M; $[N_2] = 0.042$ M; and $[H_2] = 0.042$ M

Key Takeaway

- An ICE chart is a convenient way to determine equilibrium concentrations from starting amounts.

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6.7: Predicting the Direction of a Reaction- the reaction quotient

Often you will know the concentrations of reactants and products for a particular reaction and want to know whether the system is at equilibrium. If it is not, it is useful to predict how those concentrations will change as the reaction approaches equilibrium. A useful tool for making such predictions is the **reaction quotient**, *Q*. *Q* has the same mathematical form as the equilibrium-constant expression, but *Q* is a ratio of the actual concentrations (not a ratio of equilibrium concentrations).

For example, suppose you are interested in the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \tag{6.7.1}$$

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = 245 \tag{6.7.2}$$

and you have added 0.10 mol of each gas to a container with volume 10.0 L. Is the system at equilibrium? If not, will the concentration of SO_3 be greater than or less than 0.010 mol/L when equilibrium is reached? You can answer these questions by calculating *Q* and comparing it with *Keq*. There are three possibilities:

- If *Q* = *Keq* then the actual concentrations of products (and of reactants) are equal to the equilibrium concentrations and the system is at equilibrium.
- If *Q* < *Keq* then the actual concentrations of products are less than the equilibrium concentrations; the forward reaction will occur and more products will be formed.
- If *Q* > *Keq* then the actual concentrations of products are greater than the equilibrium concentrations; the reverse reaction will occur and more reactants will be formed.

For the reaction given above,

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(\frac{0.1mol}{10L})^2}{(\frac{0.1mol}{10L})^2(\frac{0.1mol}{10L})} = 100 \tag{6.7.3}$$

(In the expression for *Q* each actual concentration is enclosed in braces {curly brackets} in order to distinguish it from the equilibrium concentrations, which, in the *Keq* expression, are enclosed in [square brackets].) In this case *Q* = 100. This is less than *Keq*, which has the value 245. This implies that the concentrations of products are less than the equilibrium concentrations (and the concentrations of reactants are greater than the equilibrium concentrations). Therefore the reaction will proceed in the forward direction, producing more products, until the concentrations reach their equilibrium values.

Example 6.7.1: Equilibrium

At 2300 K, the equilibrium constant, *Keq*, is 1.7 x 10^{-3} for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \tag{6.7.4}$$

A mixture of the three gases at 2300 K has these concentrations, $[N_2]$ = 0.17 mol dm^{-3}, $[O_2]$ = 0.17 mol dm^{-3}, and [NO] = 0.034 mol dm^{-3}.

(a) Is the system at equilibrium?

(b) In which direction must the reaction occur to reach equilibrium?

(c) What are the equilibrium concentrations of N_2, O_2, and NO?

Solution

Use the known concentrations to calculate *Q*. Compare *Q* with *Keq* to answer questions (a) and (b). Use an ICE table to answer part (c).

$$Q = \frac{\{NO\}^2}{\{N_2\}\{O_2\}} = \frac{(0.034 \text{mol dm}^{-3})^2}{(0.17 \text{mol dm}^{-3})(0.17 \text{mol dm}^{-3})} = 4.0 \times 10^{-2} \tag{6.7.5}$$

a. *Q* is larger than *Keq*, so the reaction is not at equilibrium.

b. Because *Q* is larger than *Keq*, the concentration of the product, NO, is larger than its equilibrium concentration and the concentrations of the reactants, N_2 and O_2, are smaller than their equilibrium concentrations. Therefore some of the product, NO, will be consumed and more of the reactants, N_2 and O_2, will be formed.

c. Use the given concentrations as the initial concentrations of reactants and product. Enter these into an ICE table. Let *x* be the increase in the concentration of N_2 as the system reacts to equilibrium. The ICE table looks like this:

	N_2	O_2	NO
Initial concentration/mol dm^{-3}	0.17	0.17	0.034
Change in concentration/mol dm^{-3}	*x*	*x*	-2*x*
Equilibrium concentration/mol dm^{-3}	0.17 + *x*	0.17 + *x*	0.034 - 2*x*

Next, substitute the equilibrium concentrations into the *Keq* expression and solve for *x*.

$$K_{eq} = 1.7 \times 10^{-3} = \frac{(0.034 - 2x)^2}{(0.17 + x)(0.1 + x)} \tag{6.7.6}$$

Now take the square root of both sides of this equation. This gives

$$\sqrt{1.7 \times 10^{-3}} = 0.0412 = \frac{0.034 - 2x}{0.17 + x}$$

Multiplying both sides by 0.17 + *x* gives

$$0.0070 + 0.412x = 0.034 - 2x$$

$$2x + 0.0412x = 0.034 - 0.0070$$

$$x = \frac{0.0270}{2.0412} = 0.0132$$

$$[N_2] = [O_2] = 0.17 + 0.013 = 0.183 \text{ mol dm}^{-3}$$

$$[NO] = 0.034 - 2(0.0132) = 0.0076 \text{ mol dm}^{-3}$$

Check the result by substituting these concentrations into the equilibrium constant expression.

$$K_{eq} = \frac{(0.0076)^2}{(0.18)(0.18)} = 1.8 \times 10^{-3} \tag{6.7.7}$$

This agrees to two significant figures with the *Keq* value of 1.7 x 10^{-3}.

Contributors

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6.8: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called ***Le Chatelier's principle****: If an equilibrium is stressed, then the reaction shifts to reduce the stress.*

Although there are several ways to stress an equilibrium, as we will see below. But all the equilibrium can do is response is to shift either towards reactants or products.

Effect of changing concentrations of reactants or products

One way is to stress the equilibrium is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 6.8.1:

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction—toward reactants or toward products-—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 6.8.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

Effect of Changing Pressure

How does an equilibrium react to a change in pressure? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 6.8.2:

What is the effect on this equilibrium if pressure is increased?

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

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Exercise 6.8.2

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts toward reactants.

Effect of changing temperature

What is the effect of temperature changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic: energy + reactants → products

exothermic: reactants → products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 6.8.3:

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Exercise 6.8.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

Effect of a Catalyst

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure **6.8.1** Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 6.8.1

1. Define *Le Chatelier's principle*.
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g)$$

   a. decreased temperature
   b. increased pressure
   c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ$$

   a. increased temperature
   b. addition of H_2
   c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ$$

   a. removal of SO_3
   b. addition of O_2
   c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g)$$

   a. addition of CO
   b. increased pressure
   c. addition of a catalyst

7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.

8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2.
3.

   a. toward reactants
   b. toward reactants
   c. toward products

4.
5.

a. toward products
b. toward products
c. toward products

6.
7. increased pressure, decreased temperature, removal of NH_3

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6.9: Relationship Between Free Energy and K eq

Formation of stalactites (pointing down) and stalagmites (pointing up) is a complex process. Solutions of minerals drip down and absorb carbon dioxide as water flows through the cave. Calcium carbonate dissolves in this liquid and re-deposits on the rock as the carbon dioxide is dissipated into the environment.

Equilibrium Constant and ΔG

At equilibrium, the ΔG for a reversible reaction is equal to zero. K_{eq} relates the concentrations of all substances in the reaction at equilibrium. Through a more advanced treatment of thermodynamics, we can write the following equation:

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

The variable R is the ideal gas constant ($8.314\ \text{J/K} \cdot \text{mol}$), T is the Kelvin temperature, and $\ln K_{eq}$ is the natural logarithm of the equilibrium constant.

When K_{eq} is large, the products of the reaction are favored and the negative sign in the equation means that the ΔG° is negative. When K_{eq} is small, the reactants of the reaction are favored. The natural logarithm of a number less than one is negative, and so the sign of ΔG° is positive. The table below summarizes the relationship of ΔG° to K_{eq}:

Relationship of ΔG° and K_{eq}

Table 6.9.1: Relationship of ΔG° and K_{eq}

K_{eq}	$\ln K_{eq}$	ΔG°	**Description**
>1	positive	negative	Products are favored at equilibrium.
1	0	0	Reactants and products are equally favored.
<1	negative	positive	Reactants are favored at equilibrium.

Knowledge of either the standard free energy change or the equilibrium constant for a reaction allows for the calculation of the other. The following two sample problems illustrate each case.

Example 6.9.1

The formation of nitrogen monoxide from nitrogen and oxygen gases is a reaction that strongly favors the reactants at 25°C.

$$\text{N}_2\,(g) + \text{O}_2\,(g) \rightleftharpoons 2\text{NO}\,(g)$$

The actual concentrations of each gas would be difficult to measure, and so the K_{eq} for the reaction can more easily be calculated from the ΔG°, which is equal to $173.4\ \text{kJ/mol}$. Find the K_{eq}.

Solution:

Step 1: List the known quantities and plan the problem.

Known

- $\Delta G^{\circ} = +173.4\ \text{kJ/mol}$
- $R = 8.314\ \text{J/K} \cdot \text{mol}$
- $T = 25^{\circ}\text{C} = 298\ \text{K}$

Unknown

In order to make the units agree, the value of ΔG° will need to be converted to J/mol ($173,400\ \text{J/mol}$). To solve for K_{eq}, the inverse of the natural logarithm, e^x, will be used.

Step 2: Solve.

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$\ln K_{eq} = \frac{-\Delta G^\circ}{RT}$$
$$K_{eq} = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-173{,}400\ \text{J/mol}}{8.314\ \text{J/K·mol}(298\ \text{K})}} = 4.0 \times 10^{-31}$$

Step 3: Think about your result.

The large positive free energy change leads to a K_{eq} that is extremely small. Both lead to the conclusion that the reactants are highly favored and very few product molecules are present at equilibrium.

Example **6.9.2**

The solubility product constant (K_{sp}) of lead (II) iodide is 1.4×10^{-8} at $25°C$. Calculate ΔG° for the dissociation of lead (II) iodide in water.

$$\text{PbI}_2\,(s) \rightleftharpoons \text{Pb}^{2+}\,(aq) + 2\text{I}^-\,(aq)$$

Solution:

Step 1: List the known values and plan the problem.

Known

- $K_{eq} = K_{sp} = 1.4 \times 10^{-8}$
- $R = 8.314\ \text{J/K} \cdot \text{mol}$
- $T = 25°\text{C} = 298\ \text{K}$

Unknown

The equation relating ΔG° to K_{eq} can be solved directly.

Step 2: Solve.

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{eq} \\ &= -8.314\ \text{J/K} \cdot \text{mol}\,(298\ \text{K})\ \ln\left(1.4 \times 10^{-8}\right) \\ &= 45{,}000\ \text{J/mol} \\ &= 45\ \text{kJ/mol}\end{aligned}$$

Step 3: Think about your result.

The large, positive ΔG° indicates that the solid lead (II) iodide is nearly insoluble and so very little of the solid is dissociated at equilibrium.

Summary

- The relationship between ΔG and K_{eq} is described.
- Calculations involving these two parameters are shown.

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6.10: Nonreversible Reactions

Fires are a part of life. Some fires clear the land and allow new growth. Other fires provide warmth on a cold night. Unfortunately, many fires are destructive, leaving damage in their wake. All fires leave the environment changed, never to revert back to its original state. The carbon dioxide and water generated by a fire go off into the atmosphere and do not return. The change is permanent and irreversible.

Going to Completion

When one of the products of a reaction is removed from the chemical equilibrium system as soon as it is produced, the reverse reaction cannot establish itself and equilibrium is never reached. Reactions such as these are said to go to completion. These processes are often referred to as **non-reversible reactions**. Reactions which go to completion tend to produce one of three types of products: (1) an insoluble precipitate, (2) a gas, (3) a molecular compound such as water. Examples of these reactions are shown below.

1. Formation of a precipitate:

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s)$$

2. Formation of a gas:

$$\mathrm{Mg}\,(s) + 2\mathrm{HCl}\,(aq) \rightarrow \mathrm{MgCl_2}\,(aq) + \mathrm{H_2}\,(g)$$

3. Formation of water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

If we look at these reactions in more detail, we can see some things that are not apparent the way the equations are written. Looking at the first equation, we do not see a double arrow between reactants and products, because the reaction is considered essentially irreversible. However, if we consider the net ionic equation

$$\mathrm{Ag^+} + \mathrm{Cl^-} \rightarrow \mathrm{AgCl}$$

then the reverse reaction would be:

$$\mathrm{AgCl} \rightarrow \mathrm{Ag^+} + \mathrm{Cl^-}$$

The K_{eq} for the reverse reaction is 1.8×10^{-10}. For all practical purposes, the reaction goes to completion.

Formation of a gas in an open system is essentially irreversible since the gas escapes into the atmosphere. Looking at the activity series, we see that Mg is much higher in the series than hydrogen. So the reaction would be expected to go strongly in the indicated direction.

The third reaction gets a little more complicated. In solution, the reactants HCl and NaOH will be ionized completely, as does the NaCl product. Water exists in an equilibrium with $\mathrm{H^+}$ and $\mathrm{OH^-}$, with the dissociation constant for water being 1×10^{-14}. So, in the solution resulting from the reaction given here, the $[\mathrm{H^+}]$ is $1 \times 10^{-7}\ \mathrm{M}$, a very insignificant amount. For all practical purposes, this reaction can be said to go to completion.

Summary

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CHAPTER OVERVIEW

7: Acid and Base Equilibria

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7.1: Arrhenius Acids and Bases

Learning Objective

- Identify an Arrhenius acid and an Arrhenius base.
- Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in an aqueous solution. Classic Arrhenius acids can be considered highly polarized covalent compounds which undergo dissociation in water, producing an anion (A-) and H^+ as the cation. The H+ is usually referred to as a proton. The hydrogen atom contains one proton in the nucleus and one electron around it, so when the cation H^+ is formed, only a proton is left, and therefore its name.

$$HA(aq) \rightarrow A^-(aq) + H^+(aq)$$

Typical Arrhenius acids are hydrochloric acid and nitric acid, since they undergo the following reactions in water:

$$HCl(aq) \rightarrow Cl^-(aq) + H^+(aq)$$

$$HNO_3(aq) \rightarrow NO_3^-(aq) + H^+(aq)$$

The formation of the H^+ cation in water is responsible for all the properties of an acid.

How can a covalent compound such as HCl generate ions in solution?

In hydrogen chloride, the H-Cl single covalent bond is highly polarized, due to the difference in electronegativity between H and Cl. The chlorine atom carries a partial negative charge (ð-) while the hydrogen atom carries a partial positive charge (ð-). When hydrogen chloride is dissolved in water, the polar nature of water molecules makes water interact with these partial charges in HCl, and it favors the rupture of the H-Cl, generating Cl^- anion and H^+ cation. This type of bond dissocation in which one of the elements keeps the shared electrons and ions are produced is called **Heterolytic bond cleavage or ionization**

$$H\text{-}Cl(aq) \rightarrow Cl^-(aq) + H^+(aq)$$

The formation of these ions is also stabilized by the water, by **ion-dipole interactions**.

In order to undergo ionization producing H^+, the H atom must be attached to a highly electronegative element such as halogen (group 17 in the periodic table), or O, such as in the case of polyatomic acids, like HNO_3 (the H is attached to one of the oxygen atoms, not the N. Remember Lewis structures?)

Table **7.1.1** lists some Arrhenius acids and their names.

Table **7.1.1** Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

An **Arrhenius base** is a compound that increases the OH^- ion concentration in aqueous solution. Ionic compounds of the OH^- ion are classic Arrhenius bases. All hydroxides, such as NaOH and $Ca(OH)_2$ are considered Arrhenius bases. Hydroxides are **ionic compounds;** therefore they undergo dissociation in water producing OH- (also sometimes written as HO- to indicate that the negative charge is carried by the oxygen atom) anion:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

$$Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2\ HO^-(aq)$$

This is in line with the general properties of ionic compounds. In this case, also water molecules stabilized the formation of cations and anions by **ion-diple interactions.**

Example 7.1.1:

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

a. HNO_3
b. CH_3OH
c. $Mg(OH)_2$

Solution

a. This compound is an ionic compound between H^+ ions and NO_3^- ions, so it is an Arrhenius acid.
b. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
c. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH^- ion and is an Arrhenius base.

Exercise 7.1.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

Answer

1. Arrhenius base
2. Arrhenius acid
3. neither (the H is attached to Carbon, the bond polarity is very low)

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 7.1.1:

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

Exercise 7.1.1

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer

$2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

Key Takeaways

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

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7.2: Brønsted-Lowry Acids and Bases

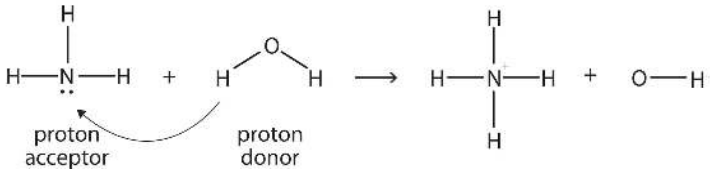
Learning Objectives

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to substances that can generate H^+ and the OH^- ions in aqueous solutions. Although this is useful because water is a common solvent, it does not explain the acidity and basicity of all substances. For example, when ammonia (NH_3) is dissolved in water, a basic solution is formed. But how can this be possible if NH_3 has no OH- in its chemical formula?

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

According to this theory, ammonia (NH3) is a base even though it does not contain OH^- ions in its formula. Instead, it generates OH^- ions as the product of a proton-transfer reaction with H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ ions and OH^- ions. Therefore, this theory explains the acidity and basicity of compounds that do not contain H^+ or HO^- in their formulas.

Relationship between Arrhenius and Brønsted-Lowry theories

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$\mathbf{HCl\,(g) + H_2O(\ell) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion**(H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O).

These two examples (NH3 in water and HCl in water) show that H_2O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

Example 7.2.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3}$$

Solution

The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Exercise 7.2.1: Aluminum Ions in Solution

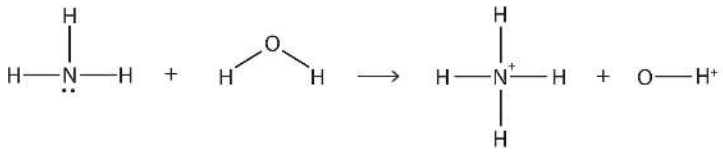
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

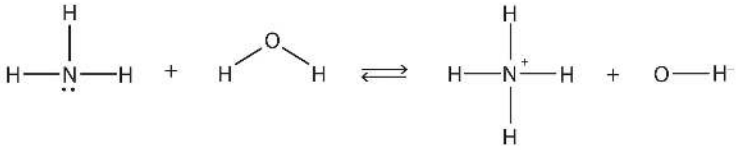
Answer

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

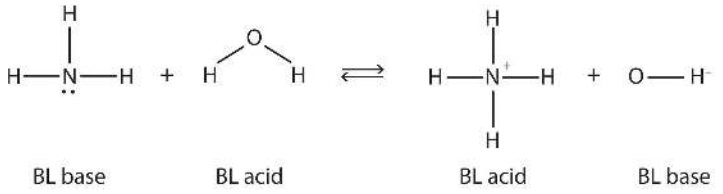
In the reaction between NH_3 and H_2O,



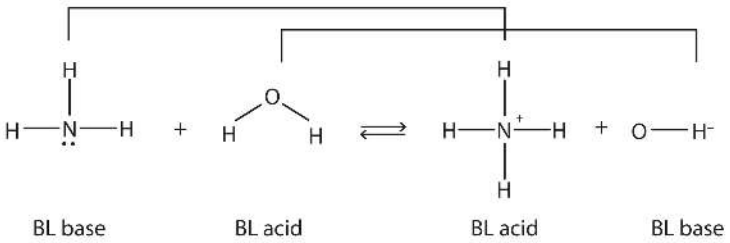
the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change of the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:



What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while the OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:



This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



The two sets—NH_3/NH_4^+ and H_2O/OH^-—are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs. One easy way to identify a conjugate acid-base pair is by looking at the chemical formulas: a conjugate acid-base pair has a H^+ difference in their formulas, i.e., NH_3/NH_4^+ or HCl/Cl^-. The acid member of the pairs always carries the H^+.

Example 7.2.2

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base. The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 7.2.2

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

Chemistry is Everywhere: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Section 4.6, vinegar was mentioned as a dilute solution of acetic acid [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O and forming excess OH^- ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, non-lye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.



Figure **7.2.1** Drain Cleaners. Drain cleaners can be made from a reactive material that is less caustic than a base. Source: Photo used by permission of Citrasolv, LLC.

Key Takeaways

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

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7.3: Names and Formulas of Acids

Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H^+) when dissolved in water.



Figure **7.3.1**: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like $NaCl$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$HCl \rightarrow H^+ + Cl^- \tag{7.3.1}$$

Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic.

Naming Binary acids (in aqueous form)

A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. The acid name begins with the prefix *hydro-*. followed by the base name of the anion, followed by the suffix *-ic*.

Hydro- and Base name of Non metal and *-ic + acid*

Example: $HCl_{(aq)}$

Cl^-, chloride ion

hydrochloric acid

Naming Oxyacids

An **oxyacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

a. Oxyanions with ***-ite*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.

Base name of oxyanion and *-ous+ acid*

Example: $H_2SO_{3(aq)}$

SO_3^{2-}, sulfite ion

sulfurous acid

b. Oxyanions with ***-ate*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ic***. There is no prefix.

Base name of oxyanion and *-ic+ acid*

Example: $H_3PO_{4(aq)}$

PO_4^{3-} phosphate ion

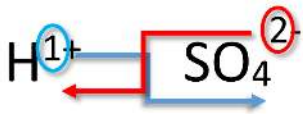
phosphoric acid

Note

The base name for sulfur containing oxyacid is ***sulfur-*** instead of just ***sulf-***. The same is true for a phosphorus containing oxyacid. The base name is ***phosphor-*** instead of simply ***phosph-***.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the $\mathbf{H^+}$ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.



Formula: H_2SO_4

***Figure* 7.3.2:** *Crisscross approach to writing formula for sulfuric acid.*

Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.

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7.4: Names and Formulas of Bases

Bases

A **base** can be simply defined as an ionic compound that produces **hydroxide ions** when dissolved in water. One of the most commonly used bases is sodium hydroxide, illustrated below.

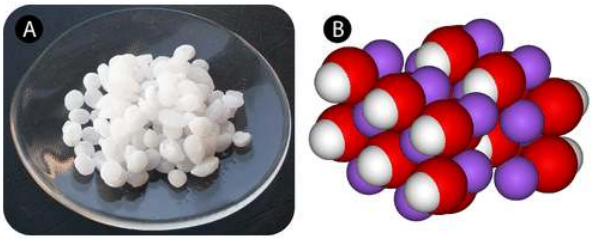


Figure 7.4.1: (A) Sodium hydroxide, a base, is a solid that is typically produced as small white pellets. (B) The structure of sodium hydroxide is an extended three-dimensional network. The purple spheres are the sodium ions (Na^+). The red and white spheres are oxygen and hydrogen atoms, respectively, which are bonded together to form hydroxide ions (OH^-).

Some bases do not contain hydroxide, but they can react with water, accepting an H^+, and producing OH^-. Ammonia is an example of such a base:

$NH_3(g) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

Names and Formulas of Bases

There is no special system for naming bases. Since they all contain the OH^- anion, names of bases end in *hydroxide*. The cation is simply named first. Some examples of names and formulas for bases are shown in the table below.

Table 7.4.1

Formula	Name
$NaOH$	sodium hydroxide
$Ca(OH)_2$	calcium hydroxide
NH_4OH	ammonium hydroxide
NH_3	ammonia
$Fe(OH)_2$	Iron(II) hydroxide or Ferrous hydroxide
$Fe(OH)_3$	Iron(III) hydroxide or Ferric hydroxide

Notice that because hydroxides are ionic compounds, the number of hydroxides in the formula does not affect the name. The compound must be neutral, so the charges of the ions are balanced just as for other ionic compounds. The sodium ion (Na^+) requires one OH^- ion to balance the charge, so the formula is $NaOH$. Calcium (Ca^{2+}) requires two OH^- ions to balance the charge, so the formula is $Ca(OH)_2$. Hydroxide ion is a polyatomic ion, and must be in parentheses when there is more than one in a formula.

Concentrated aqueous solutions of ammonia (NH_3) contain significant amounts of the hydroxide ion, even though the dissolved substance is not primarily ammonium hydroxide (NH_4OH) as is often stated on the label. Thus aqueous ammonia solution is also a common base.

For transition metals, more than one cation is possible. In this case, the name of the hydroxide includes the charge of the cation in roman numerals and parenthesis. For example, iron can form two possible cattions: Fe^{2+} or Fe^{3+}, and therefore, two hydroxides are possible: iron(II) hydroxide with formula $Fe(OH)_2$, or iron(III) hydroxide with formula $Fe(OH)_3$. Alternatively, a classic

nomenclature system uses the root name of the metal in Latin plus the ending *-ous* to refer to the lowest possible charge, and the *-ic* ending to refer to the highest possible charge. In this system, $Fe(OH)_2$ and $Fe(OH)_3$ are named Ferrous hydroxide and Ferric hydroxide, respectively.

Summary

- Bases are ionic compounds that produce hydroxide ions when dissolved in water.
- The cation is named first followed by *hydroxide*. When more than one cation is possible, the charge of the ion in roman numerals must be included.

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7.5: Autoionization of Water

Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H^+ and OH^- in solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ } (H_2O \text{ acts as an acid})$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ } (H_2O \text{ acts as a base})$$

It may not be surprising to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both $H^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of $H^+(aq)$—$[H^+]$—is greater than 1.0×10^{-7} M, while for bases the concentration of $OH^-(aq)$—$[OH^-]$—is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations—$[H^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_W:

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$, you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_W.

Example 7.5.1:

What is $[OH^-]$ of an aqueous solution if $[H^+]$ is 1.0×10^{-4} M?

Solution

Using the expression and known value for K_W,

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4}:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

Exercise 7.5.1

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer

1.0×10^{-5} M

Summary

In any aqueous solution, the product of [H+] and [OH−] equals $\mathbf{1.0 \times 10^{-14}}$ (at room temperature).

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7.6: The pH and pOH Scales

Learning Objectives

- Define *pH*.
- Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H^+]$ (or $[H_3O^+]$)

$$pH = -\log[H^+] \text{ or } pH = -\log [H_3O^+]$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale and is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

Since in solution, $[H^+] = [H_3O^+]$, we can used both expression indistinctly. For simplicity, we will use $[H^+]$.

Example 7.6.1:

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 7.6.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

Answers

1. basic
2. basic
3. acidic

Table **7.6.1** gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table **7.6.1** Typical pH Values of Various Substances*

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
*Actual values may vary depending on conditions	

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH, it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

The pOH scale

In the same way that we used $[H^+]$ to define pH, alternatively, we could use $[OH^-]$ to define pOH:

$$pH = -\log [OH^-]$$

and

$$[OH^-] = 10^{-pOH}$$

The pOH scale also ranges from 0 to 14 values, and it can be used to describe the acidity or basicity of a solution. However, *pOH scale is not commonly used* and we will always use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

Key Takeaways

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

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7.7: pH Calculations, pH measurement, and pH estimation

Calculations involving proton (H^+) (or hydronium ion,H_3O^+) concentrations are generally done using *logarithms*. Recall that a **logarithm** is simply the exponent that some base number needs to be raised to in order to generate a given number. In these calculations, we will use a base of 10. A number such as 10,000 can be written as 10^4, so by the definition, the logarithm of 10^4 is simply 4. For a small number such as 10^{-7}, the logarithm is again simply the exponent, or -7.

There is one other convention that chemists apply when they are dealing with logarithms of hydronium ion concentrations, that is, the logarithm is multiplied by (-1) to change its sign. Why would we do this? In most aqueous solutions, $[H^+]$ will vary between 10^{-1} and 10^{-13} M, giving logarithms of –1 to –13. To make these numbers easier to work with, we take the *negative* of the logarithm ($-\log[H^+]$) and call it a ***p*H** value. The use of the lower-case "*p*" reminds us that we have taken the *negative* of the logarithm, and the upper-case "H" tells us that we are referring to the *hydronium ion concentration.* Converting a hydronium ion concentration to a *p*H value is simple. Suppose you have a solution where $[H^+] = 3.46 \times 10^{-4}$ M and you want to know the corresponding *p*H value. You would enter 3.46×10^{-4} into your calculator and press the LOG button. The display should read "-3.460923901". First, we multiply this by (-1) and get 3.460923901. Next, we examine the number of significant figures. Our experimental number, 3.46×10^{-4} has three significant figures, so our mantissa must have three digits. We round our answer and express our result as, *p*H = 3.461.

The reverse process is equally simple. If you are given a *p*H value of 7.04 and are asked to calculate a hydronium ion concentration, you would first multiply the *p*H value by (-1) to give –7.04. Enter this in your calculator and then press the key (or key combination) to calculate "10^x"; your display should read "9.120108×10^{-8}". There are only two digits in our original mantissa (7.**04**) so we must round this to *two* significant figures, or $[H_3O^+] = 9.1 \times 10^{-8}$.

Exercise 7.7.1

Calculating $[H_3O^+]$ and pH Values

1. A solution is known to have a proton (hydronium ion) concentration of 4.5×10^{-5} M; what is the *p*H this solution?
2. A solution is known to have a *p*H of 9.553; what is the concentration of hydronium ion in this solution?
3. A solution is known to have a hydronium ion concentration of 9.5×10^{-8} M; what is the *p*H this solution?
4. A solution is known to have a pH of 4.57; what is the hydronium ion concentration of this solution?

There is another useful calculation that we can do by combining what we know about *p*H and expression

$$K_W = [H^+][HO^-] \tag{7.7.1}$$

We know that $K_W = 10^{-14}$ and we know that ($-\log [H_3O^+]$) is *p*H. If we define ($-\log [HO^-]$) as *p*OH, we can take our expression for K_W and take the (-log) of both sides (remember, algebraically you can perform the same operation on both sides of an equation) we get:

$$K_W = 10^{-14} = [H^+][HO^-] \tag{7.7.2}$$

$$-\log(10^{-14}) = (-\log[H^+]) + (-\log[HO^-]) \tag{7.7.3}$$

$$14 = pH + pOH \tag{7.7.4}$$

Which tells us that the values of *p*H and *p*OH must always add up to give 14! Thus, if the *p*H is 3.5, the *p*OH must be 14 – 3.5 = 11.5. This relationship is quite useful as it allows you to quickly convert between *p*H and *p*OH, and therefore between $[H_3O^+]$ and $[HO^-]$.

The simplest way to **measure the *p*H** of a solution is to use an electronic ***p*H meter.** A *p*H meter is actually a sensitive millivolt meter that measures the potential across a thin, sensitive glass electrode that is immersed in the solution. The voltage that develops is a direct function of the *p*H of the solution and the circuitry is calibrated so that the voltage is directly converted into the equivalent of a *p*H value. You will most likely use a simple *p*H meter in the laboratory. The thing to remember is that the sensing electrode has a very thin, fragile, glass membrane and is somewhat expensive to replace. Be careful!



A simple pH meter. Image by Ildar Sagdejev (Specious), CC BY-SA 4.0, via Wikimedia Commons.

A simple way to **estimate the *p*H** of a solution is by using an *indicator.* A ***p*H indicator** (see section 7.21: Indicators) is a compound that undergoes a change in color at a certain *p*H value. For example, phenolphthalein is a commonly used indicator that is *colorless* at *p*H values below 9, but is *pink* at *p*H 10 and above (at very high *p*H it becomes colorless again). In the laboratory, a small amount of phenolphthalein is added to a solution at low *p*H and then a base is slowly added to achieve neutrality. When the phenolphthalein changes from colorless to pink, you know that enough base has been added to neutralize all of the acid that is present. In reality, the transition occurs at *p*H 9.2, not *p*H 7, so the resulting solution is actually slightly alkaline, but the additional hydroxide ion concentration at pH 9 (10^{-5} M) is generally insignificant relative to the concentrations of the solutions being tested.

Another convenient way to **estimate the *p*H** of a solution is to use ***p*H paper.** This is simply a strip of paper that has a mixture of indicators embedded in it. The indicators are chosen so that the paper takes on a slightly different color over a range of *p*H values. The simplest *p*H paper is *litmus paper* that changes from pink to blue as a solution goes from acid to base. Other *p*H papers are more exotic. In the laboratory, you will use both indicators, like phenolphthalein, and *p*H papers in neutralization experiments called *titrations.*

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7.8: Properties of Acids

A cup of coffee first thing in the morning can help start the day. However, keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee!

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food.

Acids are a distinct class of compounds because of the properties of their aqueous solutions. These properties are:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g)$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Summary

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7.9: Properties of Bases

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the **HCl** in the stomach and neutralize it, taking care of that unpleasant feeling.

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.



Figure* 7.9.1*: *Phenolphthalein indicator in presence of base.*

Please note that tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words, don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate.

Summary

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7.10: Strong and Weak Acids and Acid Ionization Constant (K a)

Etching of glass is a slow process that can produce beautiful artwork. Traditionally, the glass has been treated with dilute hydrofluoric acid which gradually dissolves the glass under it. Parts of the piece that should not be etched are covered with wax or some other non-reactive material. In more recent times, compounds such as ammonium bifluoride have been used. Whichever chemical is employed, the artist must be very careful not to get any on their skin.

Strong and Weak Acids and Acid Ionization Constant

Acids are classified as either strong or weak, based on their ionization in water. A **strong acid** is an acid which is completely ionized in an aqueous solution. Hydrogen chloride (HCl) ionizes completely into hydrogen ions and chloride ions in water.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq) \tag{7.10.1}$$

A **weak acid** is an acid that ionizes only slightly in an aqueous solution. Acetic acid (found in vinegar) is a very common weak acid. Its ionization is shown below.

$$\mathrm{CH_3COOH}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{CH_3COO^-}\,(aq) \tag{7.10.2}$$

The ionization of acetic acid is incomplete, and so the equation is shown with a double arrow. The extent of ionization of weak acids varies, but is generally less than 10%. A $0.10\ \mathrm{M}$ solution of acetic acid is only about 1.3% ionized, meaning that the equilibrium strongly favors the reactants.

Weak acids, like strong acids, ionize to yield the $\mathrm{H^+}$ ion and a conjugate base. Because HCl is a strong acid, its conjugate base ($\mathrm{Cl^-}$) is extremely weak. The chloride ion is incapable of accepting the $\mathrm{H^+}$ ion and becoming HCl again. In general, the stronger the acid, the weaker its conjugate base. Likewise, the weaker the acid, the stronger its conjugate base.

Table 7.10.1: Relative Strengths of Acids and their Conjugate Bases

Acid	Conjugate Base
Strong Acids	
HCl (hydrochloric acid) (strongest)	$\mathrm{Cl^-}$ (chloride ion) (weakest)
$\mathrm{H_2SO_4}$ (sulfuric acid)	$\mathrm{HSO_4^-}$ (hydrogen sulfate ion)
$\mathrm{HNO_3}$ (nitric acid)	$\mathrm{NO_3^-}$ (nitrate ion)
Weak Acids	
$\mathrm{H_3PO_4}$ (phosphoric acid)	$\mathrm{H_2PO_4^-}$ (dihydrogen phosphate ion)
$\mathrm{CH_3COOH}$ (acetic acid)	$\mathrm{CH_3COO^-}$ (acetate ion)
$\mathrm{H_2CO_3}$ (carbonic acid)	$\mathrm{HCO_3^-}$ (hydrogen carbonate ion)
HCN (hydrocyanic acid) (weakest)	$\mathrm{CN^-}$ (cyanide ion) (strongest)

Strong acids are 100% ionized in solution. Weak acids are only slightly ionized. Phosphoric acid is stronger than acetic acid and so is ionized to a greater extent. Acetic acid is stronger than carbonic acid, and so on.

The Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:

$$\mathrm{HA}\,(aq) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq) \tag{7.10.3}$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \tag{7.10.4}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially **100%** ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table **7.10.2**: Acid Ionization Constants at **25°C**

Name of Acid	Ionization Equation	K_a	pK_a
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$	very large 1.3×10^{-2}	pK_{a1} >>>>1 pK_{a2} =1.89
Oxalic acid	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ $HC_2O_4 \rightleftharpoons H^+ + C_2O_4^{2-}$	6.5×10^{-2} 6.1×10^{-5}	pK_{a1} = 1.18 pK_{a2} = 4.21
Phosphoric acid	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2--}$ $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	7.5×10^{-3} 6.2×10^{-8} 4.8×10^{-13}	pK_{a1} = 2.12 pK_{a2} = 7.20 pK_{a3} = 12.32
Hydrofluoric acid	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}	pK_a = 3.15
Nitrous acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}	pK_a = 3.35
Benzoic acid	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.5×10^{-5}	pK_a = 4.18
Acetic acid	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	pK_a = 4.74
Carbonic acid	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}	pK_{a1} = 6.40 pK_{a2} = 10.32
Hydrocyanic acid	$HCN \rightleftharpoons H^+ + CN^-$	4.9×10^{-10}	pK_a = 9.31

pK_a values

Because K_a values are usually very small numbers, sometimes chemists prefer to work with pK_a values, that is:

pKa = -log Ka

Table **7.10.2** shows the pK_a values for several bases. *Notice that the stronger the acid, the higher the Ka values but the lower its pK_a.*

Summary

- Strong and weak acids are defined.
- The acid ionization constant (K_a) and pK_a are defined.
- The stronger the acid, the higher the Ka values but the lower its pK_a.

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7.11: Strong and Weak Bases and Base Ionization Constant (K b)

All the complex electronics and apparatus in a space shuttle generate heat, as do the astronauts. The shuttles have a complex arrangement of systems to dissipate that heat into outer space. One of the components of this system is a series of coils filled with ammonia that are located on the outside of the shuttle. Ammonia absorbs the heat and then releases it into space as the gas circulates through the coils. This approach is both inexpensive and effective.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq) \tag{7.11.1}$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[NH_4{}^+]\,[OH^-]}{[NH_3]} \tag{7.11.2}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. The table below is a listing of base ionization constants for several weak bases.

Notice that the conjugate base of a weak acid is also a strong base. For example, the acetate ion has a small tendency to accept a hydrogen ion from water to form acetic acid and the hydroxide ion.

Table 7.11.1: Base Ionization Constants at 25°C

Name of Base	Ionization Equation	K_b	pKb
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3{}^+ + OH^-$	5.6×10^{-4}	3.25
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$	1.8×10^{-5}	4.74
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}	8.77
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}	9.25
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}	10.85
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3{}^+ + OH^-$	1.5×10^{-14}	13.82

pK_b values

Because Kb values are usually very small numbers, sometimes chemists prefer to work with pK_b values, that is:

$pK_b = -\log K_b$

Table **7.11.1** shows the pK_b values for several bases. *Notice that the stronger the base, the higher the K_b values but the lower its pK_b.*

Summary

- Strong and weak bases are defined.
- The base equilibrium constant K_b and pK_b are stated.
- The stronger the base, the higher the K_b values but the lower its pK_b.

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7.12: Relationship between Ka, Kb, pKa, and pKb

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{7.12.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[HA]} \tag{7.12.2}$$

The equilibrium constant for this reaction is the acid ionization constant K_a, also called the acid dissociation constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{7.12.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 7.12.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H^3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them **unitless**. The values of K_a for a number of common acids are given in Table 7.12.1.

Table 7.12.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^{9}	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^{2}	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^{1}	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{7.12.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{7.12.5}$$

Once again, the concentration does not appear in the equilibrium constant expression.. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 7.12.2.

Table 7.12.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00

*As in Table 7.12.1.

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{7.12.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{7.12.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{7.12.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{7.12.9}$$

If we add Equations 7.12.6 and 7.12.7, we obtain the following (recall that the equilibrium constant for the sum of two reactions is the product of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} / \cancel{[HCN]} \tag{7.12.10}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} / \cancel{[CN^-]} \tag{7.12.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{7.12.12}$$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{7.12.13}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{7.12.14}$$

$$K_a = 10^{-pK_a} \tag{7.12.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{7.12.16}$$

$$K_b = 10^{-pK_b} \tag{7.12.17}$$

Similarly, Equation 16.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{7.12.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{7.12.19}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 16.5.1 and Table 16.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.5.2 are the common strong acids; at the top right are the most common strong bases. **Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.**

> The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base} \tag{7.12.20}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{7.12.21}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-} \tag{7.12.22}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{7.12.23}$$

> All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 7.12.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.5.15 and Equation 16.5.16. Use the relationships pK = −log K and K = 10−pK (Equation 16.5.11 and Equation 16.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.5.16: pK_a + pK_b = pKw = 14.00. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00 \tag{7.12.24}$$

$$pK_b = 14.00 - 4.83 = 9.17 \tag{7.12.25}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14} \tag{7.12.26}$$

$$K_a = 1.9 \times 10^{-11} \tag{7.12.27}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27 \tag{7.12.28}$$

$$pKa + pK_b = 14.00 \tag{7.12.29}$$

$$pK_a = 10.73 \tag{7.12.30}$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11} \tag{7.12.31}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 7.12.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

$K_a = 1.4 \times 10^{-4}$ for lactic acid;

pK_b = 10.14 and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Summary

Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the

dissociation constant is called the acid ionization constant (Ka). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (Kb). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair.

Key Takeaways

- The Ka and Kb values for a conjugated acid–base pairs are related through the K_w value:

$$K_aK_b = K_w \tag{7.12.32}$$

- The conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{7.12.33}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{7.12.34}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w \tag{7.12.35}$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a} \tag{7.12.36}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b} \tag{7.12.37}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w \tag{7.12.38}$$

$$pK_a + pK_b = 14.00 \text{ at } 25°C \tag{7.12.39}$$

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7.13: Calculating Ka and Kb

The pH meter was invented because Florida orange growers needed a way to test the acidity of their fruit. The first meter was invented by Arnold Beckman, who went on to form Beckman Instruments. Beckman's business was very successful, and he used much of his fortune to fund science education and research. The Beckman family donated $40 million to build the Beckman Institute at the University of Illinois.

Calculating K_a and K_b

The numerical value of K_a and K_b can be determined from an experiment. A solution of known concentration is prepared and its pH is measured with an instrument called a **pH meter**.



Figure 7.13.1: A pH meter is a laboratory device that provides quick, accurate measurements of the pH of solutions. (CC BY-NC; CK-12)

Example 7.13.1

A $0.500\ \text{M}$ solution of formic acid is prepared and its pH is measured to be 2.04. Determine the K_a for formic acid.

Solution

Step 1: List the known values and plan the problem.

Known

- Initial $[\text{HCOOH}] = 0.500\ \text{M}$
- $\text{pH} = 2.04$

Unknown

First, the pH is used to calculate the $[\text{H}^+]$ at equilibrium. An ICE table is set up in order to determine the concentrations of HCOOH and HCOO^- at equilibrium. All concentrations are then substituted into the K_a expression and the K_a value is calculated.

Step 2: Solve.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.04} = 9.12 \times 10^{-3}\ \text{M}$$

Since each formic acid molecule that ionizes yields one H^+ ion and one formate ion (HCOO^-), the concentrations of H^+ and HCOO^- are equal at equilibrium. We assume that the initial concentrations of each ion are zero, resulting in the following ICE table.

	HCOOH	H^+	HCOO^-
Initial	0.500	0	0
Change	-9.12×10^{-3}	$+9.12 \times 10^{-3}$	$+9.12 \times 10^{-3}$
Equilibrium	0.491	9.12×10^{-3}	9.12×10^{-3}

Now, substituting into the K_a expression gives:

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(9.12 \times 10^{-3})(9.12 \times 10^{-3})}{0.491} = 1.7 \times 10^{-4}$$

Step 3: Think about your result.

The value of K_a is consistent with that of a weak acid. Two significant figures are appropriate for the answer, since there are two digits after the decimal point in the reported pH.

Similar steps can be taken to determine the K_b of a base. For example, a $0.750\ M$ solution of the weak base ethylamine ($C_2H_5NH_2$) has a pH of 12.31.

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$$

Since one of the products of the ionization reaction is the hydroxide ion, we need to first find the $[OH^-]$ at equilibrium. The pOH is $14 - 12.31 = 1.69$. The $[OH^-]$ is then found from $10^{-1.69} = 2.04 \times 10^{-2}\ M$. The ICE table is then set up as shown below.

	$C_2H_5NH_2$	$C_2H_5NH_3^+$	OH^-
Initial	0.750	0	0
Change	-2.04×10^{-2}	$+2.04 \times 10^{-2}$	$+2.04 \times 10^{-2}$
Equilibrium	0.730	2.04×10^{-2}	2.04×10^{-2}

Substituting into the K_b expression yields the K_b for ethylamine.

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(2.04 \times 10^{-2})(2.04 \times 10^{-2})}{0.730} = 5.7 \times 10^{-4}$$

Summary

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7.14: Calculating pH of Strong Acid and Base Solutions

Learning Objectives

- Give the names and formulas of some strong acids and bases.
- Explain the pH scale, and convert pH and concentration of hydronium ions.
- Evaluate solution pH and pOH of strong acids or bases.

Acids and bases that are completely ionized when dissolved in water are called **strong acids** and **strong bases** There are only a few strong acids and bases, and everyone should know their names and properties. These acids are often used in industry and everyday life. The concentrations of acids and bases are often expressed in terms of pH, and as an educated person, you should have the skill to convert concentrations into pH and pOH. The pH is an indication of the hydrogen ion concentration, $[H^+]$.

Strong Acids

Strong acids are acids that are completely or nearly 100% ionized in their solutions; Table **7.14.1** includes some common strong acids. Hence, the ionization in Equation 7.14.1 for a strong acid HA can be represented with a single arrow:

$$HA\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + A^-\,(aq) \tag{7.14.1}$$

Water is the base that reacts with the acid **HA**, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. By definition, a strong acid yields 100% of H_3O^+ and A^- when the acid ionizes in water. Table **7.14.1** lists several strong acids.

Table **7.14.1**: Some of the common strong acids and bases are listed here.

Strong Acids	Strong Bases
perchloric acid ($HClO_4$)	lithium hydroxide ($LiOH$)
hydrochloric acid (HCl)	sodium hydroxide ($NaOH$)
hydrobromic acid (HBr)	potassium hydroxide (KOH)
hydroiodic acid (HI)	calcium hydroxide ($Ca(OH)_2$)
nitric acid (HNO_3)	strontium hydroxide ($Sr(OH)_2$)
sulfuric acid (H_2SO_4)	barium hydroxide ($Br(OH)_2$)

For a strong acid, $[H^+]$ = $[A^-]$ = concentration of acid if the concentration is much higher than $1 \times 10^{-7}\,M$. However, for a very dilute strong acid solution with concentration less than $1 \times 10^{-7}\,M$, the pH is dominated by the **autoionization of water**

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7.14.2}$$

Example 7.14.1

Calculate the pH of a solution with $1.2345 \times 10^{-4}\ M HCl$, a strong acid.

Solution

The solution of a strong acid is completely ionized. That is, this equation goes to completion

$$HCl\,(aq) \longrightarrow H\,(aq) + Cl^-\,(aq)$$

Thus, $[H^+] = 1.2345 \times 10^{-4}$.

$$pH = -\log(1.2345 \times 10^{-4}) = 3.90851$$

Exercise 7.14.1

What is the pH for a solution containing 0.234 M $[HCl]$?

Answer

pH = 0.63

Strong Bases

Strong bases are completely ionized in solution. Table **7.14.1** includes some common strong bases. For example, **KOH** dissolves in water in the reaction

$$\mathrm{KOH} \rightarrow \mathrm{K^+ + OH^-}$$

Relative to the number of strong acids, there are fewer number of strong bases and most are alkali hydroxides. Calcium hydroxide is considered a strong base, because it is completely, almost completely, ionized. However, the solubility of calcium hydroxide is very low. When $\mathrm{Ca(OH)_2}$ dissolves in water, the ionization reaction is as follows:

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+} + 2\,OH^-}$$

Because of the stoichiometry of calcium hydroxide, upon dissociation, the concentration of $\mathrm{OH^-}$ will be twice the concentration of $\mathrm{Ca^{2+}}$:

$$[\mathrm{OH^-}] = 2[\mathrm{Ca^{2+}}]$$

Example 7.14.4

Calculate the pH of a solution containing $1.2345 \times 10^{-4}\ M\ \mathrm{Ca(OH)_2}$.

Solution

Based on complete ionization of

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{+2} + 2\,OH^-}$$

$$\begin{aligned}[\mathrm{OH^-}] &= 2 \times 1.2345 \times 10^{-4} \\ &= 2.4690 \times 10^{-4}\ M \\ \mathrm{pOH} &= -\log(2.4690 \times 10^{-4}) \\ &= 3.6074\end{aligned}$$

$$pH = 14 - pOH \tag{7.14.3}$$

$$pH = 14 - 3.6074 \tag{7.14.4}$$

$$pH = 10.39 \tag{7.14.5}$$

Exercise 7.14.4

The molar solubility of calcium hydroxide is 0.013 M $\mathrm{Ca(OH)_2}$. Calculate the pH.

Answer

pOH = 12.42

Questions

1. What is the pH of a solution containing 0.01 M $\mathrm{HNO_3}$?
2. What is the pH of a solution containing 0.0220 M $\mathrm{Ba(OH)_2}$? Give 3 significant figures.
3. Exactly 1.00 L solution was made by dissolving 0.80 g of **NaOH** in water. What is $[\mathrm{H^+}]$? (Atomic mass: **Na**, 23.0; **O**, 16.0; **H**, 1.0)
4. What is the pH for a solution which is 0.050 M **HCl**?
5. Which of the following is usually referred to as strong acid in water solution?

$$\mathrm{HF},\ \mathrm{HNO_2},\ \mathrm{H_2CO_3},\ \mathrm{H_2S},\ \mathrm{HSO_4^-},\ \mathrm{Cl^-},\ \mathrm{HNO_3},\ \mathrm{HCN}$$

Solutions

1. ***Answer*** 2

   Hint...

   You do not need a calculator to evaluate $-\log(0.01) = 2$

2. ***Answer*** 12.64

   Hint...

   $\mathrm{Ba(OH)_2 \rightarrow Ba^{2+} + 2\,OH^-}$

3. ***Answer*** 5.0×10^{-13}

   Hint...

   $[\mathrm{OH^-}] = \frac{0.80}{40} = 0.020\ \mathrm{M}$; $[H^+] = \frac{1.0 \times 10^{-14}}{0.020} = 5 \times 10^{-13} M$. The pH is 12.30.

4. ***Answer*** 1.3

   Hint...

   This solution contains 1.83 g of HCl per liter. $[\mathrm{H^+}] = 0.050$.

5. ***Answer*** $\mathrm{HNO_3}$

   Consider...

   All others are weak acids

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7.15: Calculating pH of Weak Acid and Base Solutions

Calculating pH of Weak Acid and Base Solutions

The K_a and K_b values have been determined for a great many acids and bases, as shown in Tables 21.12.2 and 21.13.1. These can be used to calculate the pH of any solution of a weak acid or base whose ionization constant is known.

Example 7.15.1

Calculate the pH of a $2.00\ \text{M}$ solution of nitrous acid (HNO_2). The K_a for nitrous acid is 4.5×10^{-4}.

Solution

Step 1: List the known values and plan the problem.

Known

- Initial $[\text{HNO}_2] = 2.00\ \text{M}$
- $K_a = 4.5 \times 10^{-4}$

Unknown

- pH =?

First, an ICE table is set up with the variable x used to signify the change in concentration of the substance due to ionization of the acid. Then the K_a expression is used to solve for x and calculate the pH.

Step 2: Solve.

	HNO_2	H^+	NO_2^-
Initial	2.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.00 - x$	x	x

(7.15.1)

The K_a expression and value are used to set up an equation to solve for x.

$$K_a = 4.5 \times 10^{-4} = \frac{(x)(x)}{2.00 - x} = \frac{x^2}{2.00 - x} \tag{7.15.2}$$

The quadratic equation is required to solve this equation for x. However, a simplification can be made of the fact that the extent of ionization of weak acids is small. The value of x will be significantly less than 2.00, so the "$-x$" in the denominator can be dropped.

$$4.5 \times 10^{-4} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00} \tag{7.15.3}$$

$$x = \sqrt{4.5 \times 10^{-4}\,(2.00)} = 2.9 \times 10^{-2}\ \text{M} = [\text{H}^+] \tag{7.15.4}$$

Since the variable x represents the hydrogen-ion concentration, the pH of the solution can now be calculated.

$$\text{pH} = -\log[\text{H}^+] = -\log\left[2.9 \times 10^{-2}\right] = 1.54 \tag{7.15.5}$$

Step 3: Think about your result.

The pH of a $2.00\ \text{M}$ solution of a strong acid would be equal to $-\log(2.00) = -0.30$. THe higher pH of the $2.00\ \text{M}$ nitrous acid is consistent with it being a weak acid and therefore not as acidic as a strong acid would be.

The procedure for calculating the pH of a solution of a weak base is similar to that of the weak acid in the example. However, the variable x will represent the concentration of the hydroxide ion. The pH is found by taking the negative logarithm to get the pOH, followed by subtracting from 14 to get the pH.

Summary

- The procedure for calculating the pH of a weak acid or base is illustrated.

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7.16: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq) \tag{7.16.1}$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq) \tag{7.16.2}$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq) \tag{7.16.3}$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:


This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq) \tag{7.16.4}$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \tag{7.16.5}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids, meaning that one H^+ is lost at the time. This process contrasts with the ionization of strong bases such as $Ca(OH)_2$ in which all the OH- ions are lost in a single dissociation reaction:

$$Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$$

This is because hydroxides are ionic compounds, while acids are covalent compounds.

When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \tag{7.16.6}$$

with

$$K_{\mathrm{H_2CO_3}} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7} \tag{7.16.7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \tag{7.16.8}$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[H3O+][CO3^{2}-]}{[HCO3-]} = 4.7 \times 10^{-11} \tag{7.16.9}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution.

Example 7.16.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in solution.

1. Using the customary four steps, we determine the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ produced by ionization of H_2CO_3.

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

An abbreviated table of changes and concentrations shows:

ICE Table	$\mathrm{H_2CO_3}(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O^+}(aq)$	$\mathrm{HCO_3^-}(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{\mathrm{H_2CO_3}} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[\mathrm{H_2CO_3}] = 0.033\ M$$

$$[\mathrm{H_3O^+}] = [\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$$

pH=-log[H_3O^+]=3.92

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq) \tag{7.16.10}$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq) \tag{7.16.11}$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq) \tag{7.16.12}$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. Again, using the first dissociation constant is a good approximation to calculate the pH for a solution of phosphoric acid.

Contributors and Attributions

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of Ka of the acid is significant, it is a good estimation to only consider the first dissociation constant to calculate pH

Glossary

diprotic acid
: acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base
: base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid
: acid containing one ionizable hydrogen atom per molecule

stepwise ionization
: process in which an acid is ionized by losing protons sequentially

triprotic acid
: acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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7.17: Acids-Bases Reactions- Neutralization

Neutralization reactions

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as:

$$\textbf{acid + base} \rightarrow \textbf{H}_2\textbf{O + salt}$$

Example 1:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)}$$

Neutralization reactions are an example of **irreversible double-replacement reactions,** like the ones we studied in CHE 103. The stoichiometry of the balanced neutralization equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 2:

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_{4(aq)} + KOH_{(aq)} \rightarrow H_2O_{(l)} + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_{4(aq)} + 2KOH_{(aq)} \rightarrow 2H_2O_{(l)} + K_2SO_{4(aq)}$$

Exercise

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer

$2HCl_{(aq)} + Mg(OH)_{2(aq)} \rightarrow 2H_2O_{(l)} + MgCl_{2(aq)}$; magnesium chloride

Neutralization reactions and net ionic equations

In CHE 103, we examined how ionic compounds dissociate in water. In this chapter, we also learned that acids can also undergo dissociation in water.

Thus, sodium hydroxide, NaOH, is dissolved in water, it ionizes to form the sodium cation and the hydroxide anion (HO^-).

$$\textbf{NaOH } \textit{(aq)} \rightarrow \textbf{Na}^+ \textit{ (aq)} + \textbf{HO}^- \textit{ (aq)}$$

When hydrochloric acid is dissolved in water, it ionizes to form the chloride anion and H^+:

$$\textbf{HCl } \textit{(aq)} \rightarrow \textbf{H}^+ \textit{ (aq)} + \textbf{Cl}^- \textit{ (aq)}$$

When NaCl is dissolved in water, it also ionizes to form the chloride anion and sodium cation:

$$\textbf{NaCl } \textit{(aq)} \rightarrow \textbf{Na}^+ \textit{ (aq)} + \textbf{Cl}^- \textit{ (aq)}$$

Therefore, the neutralization reaction between HCl and NaOH can be written in its **total ionic form**:

$$\mathbf{HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)}\ \text{molecular equation}$$

or

$$\mathbf{Na^+\,(aq) + HO^-\,(aq) + H^+\,(aq) + Cl^-\,(aq) \rightarrow H_2O(l) + Na^+\,(aq) + Cl^-\,(aq)}\ \text{total ionic equation}$$

If we cancel the ions that do not change from reactants to products, we are left with the **net ionic equation**:

$$\mathbf{HO^-\,(aq) + H^+\,(aq) \rightarrow H_2O(l)}\ \text{net ionic equation}$$

We have written this equation using a single arrow because sodium hydroxide is a *strong base* and is essentially 100% ionized in solution. The hydroxide anion (HO^-) reacts with the hydronium ion (H_3O^+) to form *two* moles of water, as shown in the equation given below.

$$\mathbf{HCl\,(aq) + NaOH\,(aq) \rightarrow H_2O + NaCl\,(aq)}$$

Thus, we can see that the net reaction in a neutralization is the formation of water from H+ and HO- ions. This is the case no matter the nature of the acid or the base.

Exercise

Write a balanced molecular equation, a total ionic equation, and a net ionic equation for the reaction between HNO_3 acid and $Ca(OH)_2$

Answer

Molecular equation: $2HNO_3(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(NO_3)_2(aq)$

Total ionic equation: $2H^+(aq) + 2NO_3^-\,(aq) + Ca^{2+}\,(aq) + 2HO^-\,(aq) \rightarrow 2\,H_2O(l) + Ca^{2+}\,(aq) + 2NO_3^-\,(aq)$

Net ionic equation: $2H^+(aq) + 2HO^-\,(aq) \rightarrow 2\,H_2O(l)$

Using neutralization reactions to obtain salts

As described above, salts can be obtained by neutralization reactions. Since salts are ionic compounds, their boiling points are much higher than water. So after the neutralization reaction is performed using equimolar quantities of acid and base, the water can be evaporated, resulting in solid salts.

Therefore, we can use our discussion above to decide on a combination of acid and base that will result in a specific salt. For example, what acid and base could result in the formation of NaCl by neutralization?

NaCl can be dissociated into cation and anion:

$$\mathbf{NaCl\,(aq) \rightarrow Na^+\,(aq) + Cl^-\,(aq)}$$

As we have seen above, the cation always derives from the hydroxide (base) in the neutralization reaction. To reform this hydroxide, we need to add HO^- to the cation. In other words:

$$\mathbf{Na^+\,(aq) + HO^-\,(aq) \rightarrow NaOH\,(aq)}$$

The anion always derives from the acid in the neutralization reaction. To reform this acid, we need to add H^+ to the anion. In other words:

$$\mathbf{Cl^-(aq) + H^+\,(aq) \rightarrow HCl\,(aq)}$$

Therefore the acid and base that result in the formation of sodium chloride by neutralization reaction are:

$$\mathbf{HCl\,(aq) + NaOH\,(aq) \rightarrow H_2O + NaCl\,(aq)}$$

Exercise **7.17.1**

1. For each of the following, write a balanced neutralization equation:

a. The reaction of calcium hydroxide with hydrochloric acid.
b. The reaction of sodium hydroxide with sulfuric acid (both ionizations).
c. The reaction of barium hydroxide with nitric acid.

2. Write a balanced neutralization equation for the reaction of calcium hydroxide with sulfuric acid
3. What acid and base would you use to obtain the following salts by neutralization? Write a balanced neutralization reaction in each case

    a. KBr

    b. $NaNO_3$

    c. NH_4Cl

    d. MgSO4

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7.18: Titration Experiment

Titration Experiment

In the neutralization of hydrochloric acid by sodium hydroxide, the mole ratio of acid to base is 1:1.

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l) \tag{7.18.1}$$

One mole of HCl would be fully neutralized by one mole of NaOH. If instead the hydrochloric acid was reacted with barium hydroxide, the mole ratio would be 2:1.

$$2\mathrm{HCl}\,(aq) + \mathrm{Ba(OH)_2}\,(aq) \rightarrow \mathrm{BaCl_2}\,(aq) + 2\mathrm{H_2O}\,(l) \tag{7.18.2}$$

Now two moles of HCl would be required to neutralize one mole of $\mathrm{Ba(OH)_2}$. The mole ratio ensures that the number of moles of $\mathrm{H^+}$ ions supplied by the acid is equal to the number of $\mathrm{OH^-}$ ions supplied by the base. This must be the case for neutralization to occur. The **equivalence point** is the point in a neutralization reaction where the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

In the laboratory, it is useful to have an experiment where the unknown concentration of an acid or a base can be determined. This can be accomplished by performing a controlled neutralization reaction. A **titration** is an experiment where a volume of a solution of known concentration is added to a volume of another solution in order to determine its concentration. Many titrations are acid-base neutralization reactions, though other types of titrations can also be performed.

In order to perform an acid-base titration, the chemist must have a way to visually detect that the neutralization reaction has occurred. An **indicator** is a substance that has a distinctly different color when in an acidic or basic solution. A commonly used indicator for strong acid-strong base titrations is phenolphthalein. Solutions in which a few drops of phenolphthalein have been added turn from colorless to brilliant pink as the solution turns from acidic to basic. The steps in a titration reaction are outlined below.

1. A measured volume of an acid of unknown concentration is added to an Erlenmeyer flask.
2. Several drops of an indicator are added to the acid and mixed by swirling the flask.
3. A buret is filled with the base solution of known molarity.
4. The stopcock of the buret is opened and base is slowly added to the acid while the flask is constantly swirled to ensure mixing. The stopcock is closed at the exact point which the indicator just changes color.

The **standard solution** is the solution in a titration whose concentration is known. In the titration described above the base solution is the standard solution. It is very important in a titration to add the solution from the buret slowly so that the point at which the indicator changes color can be found accurately. The **end point** of a titration is the point at which the indicator changes color. When phenolphthalein is the indicator, the end point will be signified by a faint pink color.



Figure **7.18.1**: Phenolphthalein in basic solution. (CC BY-NC; CK-12)

Summary

- Definitions are given for equivalence point, titration, and indicator.
- The process for carrying out a titration is described.

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7.19: Titration Calculations

Titration Calculations

For a neutralization reaction with a 1:1 stoichiometric ratio between the acid and the base, at the equivalence point in a neutralization, the moles of acid are equal to the moles of base.

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l) \tag{7.19.1}$$

$$\text{moles acid} = \text{moles base} \tag{7.19.2}$$

Recall that the molarity (M) of a solution is defined as the moles of the solute divided by the liters of solution (L). So the moles of solute are therefore equal to the molarity of a solution multiplied by the volume in liters.

at the equivalence point :

$$\text{moles solute} = \mathrm{M} \times \mathrm{L} \tag{7.19.3}$$

We can then set the moles of acid equal to the moles of base.

$$\mathrm{M}_A \times \mathrm{V}_A = \mathrm{M}_B \times \mathrm{V}_B \tag{7.19.4}$$

M_A is the molarity of the acid, while M_B is the molarity of the base. V_A and V_B are the volumes of the acid and base, respectively.

Suppose that a titration is performed and $20.70\ \mathrm{mL}$ of $0.500\ \mathrm{M\ NaOH}$ is required to reach the end point when titrated against $15.00\ \mathrm{mL}$ of HCl of unknown concentration. The above equation can be used to solve for the molarity of the acid.

$$\mathrm{M}_A = \frac{\mathrm{M}_B \times \mathrm{V}_B}{\mathrm{V}_A} = \frac{0.500\ \mathrm{M} \times 20.70\ \mathrm{mL}}{15.00\ \mathrm{mL}} = 0.690\ \mathrm{M} \tag{7.19.5}$$

The higher molarity of the acid compared to the base in this case means that a smaller volume of the acid is required to reach the equivalence point.

The above equation works only for neutralizations in which there is a 1:1 ratio between the acid and the base. When the formula of the acids or the base determines a different molar ratio, then the equation above cannot be applied. In this case, we can use traditional stoichiometric calculations. The example below demonstrates the technique to solve a titration problem for a titration of sulfuric acid with sodium hydroxide, which react in a 1:2 moles ratio.

Example 7.19.1

In a titration of sulfuric acid against sodium hydroxide, $32.20\ \mathrm{mL}$ of $0.250\ \mathrm{M\ NaOH}$ is required to neutralize $26.60\ \mathrm{mL}$ of $\mathrm{H_2SO_4}$. Calculate the molarity of the sulfuric acid.

$$\mathrm{H_2SO_4}\,(aq) + 2\mathrm{NaOH}\,(aq) \rightarrow \mathrm{Na_2SO_4}\,(aq) + 2\mathrm{H_2O}\,(l) \tag{7.19.6}$$

Solution

Step 1: List the known values and plan the problem.

- Molarity $\mathrm{NaOH} = 0.250\ \mathrm{M}$
- Volume $\mathrm{NaOH} = 32.20\ \mathrm{mL}$
- Volume $\mathrm{H_2SO_4} = 26.60\ \mathrm{mL}$

Unknown

- Molarity $\mathrm{H_2SO_4} = ?$

First determine the moles of NaOH in the reaction. From the mole ratio, calculate the moles of $\mathrm{H_2SO_4}$ that reacted. Finally, divide the moles of $\mathrm{H_2SO_4}$ by its volume to get the molarity.

Step 2: Solve.

$$\text{mol NaOH} = \text{M} \times \text{L} = 0.250\ \text{M} \times 0.03220\ \text{L} = 8.05 \times 10^{-3}\ \text{mol NaOH} \tag{7.19.7}$$

$$8.05 \times 10^{-3}\ \text{mol NaOH} \times \frac{1\ \text{mol } H_2SO_4}{2\ \text{mol NaOH}} = 4.03 \times 10^{-3}\ \text{mol } H_2SO_4 \tag{7.19.8}$$

$$\frac{4.03 \times 10^{-3}\ \text{mol } H_2SO_4}{0.02660\ \text{L}} = 0.151\ \text{M } H_2SO_4 \tag{7.19.9}$$

Step 3: Think about your result.

The volume of H_2SO_4 required is smaller than the volume of NaOH because of the two hydrogen ions contributed by each molecule.

Summary

- The process of calculating concentration from titration data is described and illustrated.

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7.20: Titration Curves

The x-y plot that we know of as a graph was the brainchild of the French mathematician-philosopher Rene Descartes (1596-1650). His studies in mathematics led him to develop what was known as "Cartesian geometry", including the concept of today's graphs. The coordinates are often referred to as Cartesian coordinates.

Titration Curves

As base is added to acid at the beginning of a titration, the pH rises very slowly. Nearer to the equivalence point, the pH begins to rapidly increase. If the titration is a strong acid with a strong base, the pH at the equivalence point is equal to 7. A bit past the equivalence point, the rate of change of the pH again slows down. A **titration curve** is a graphical representation of the pH of a solution during a titration. The figure below shows two different examples of a strong acid-strong base titration curve. On the left is a titration in which the base is added to the acid, and so the pH progresses from low to high. On the right is a titration in which the acid is added to the base. In this case, the pH starts out high and decreases during the titration. In both cases, the equivalence point is reached when the moles of acid and base are equal and the pH is 7. This also corresponds to the color change of the indicator.

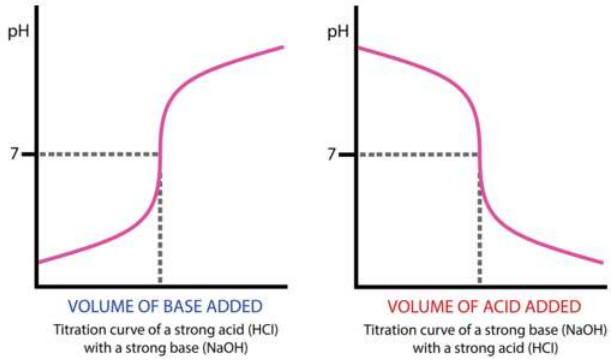


Figure **7.20.1**: A titration curve shows the pH changes that occur during the titration of an acid with a base. On the left, base is being added to acid. On the right, acid is being added to base. In both cases, the equivalence point is at pH 7. (CC BY-NC; CK-12)

Titration curves can also be generated in the case of a weak acid-strong base titration or a strong acid-weak base titration. The general shape of the titration curve is the same, but the pH at the equivalence point is different. In a weak acid-strong base titration, the pH is greater than 7 at the equivalence point. In a strong acid-weak base titration, the pH is less than 7 at the equivalence point.

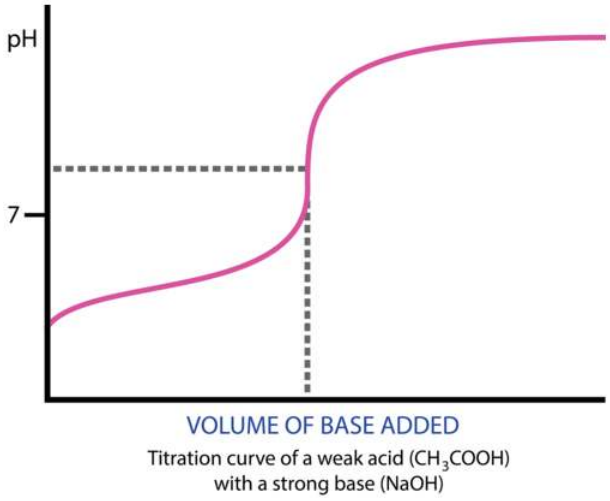


Figure **7.20.2**: Titration curve of weak acid and strong base. (CC BY-NC; CK-12)

Summary

- A titration curve is a graphical representation of the pH of a solution during a titration.
- In a strong acid-strong base titration, the equivalence point is reached when the moles of acid and base are equal and the pH is 7.

- In a weak acid-strong base titration, the pH is greater than 7 at the equivalence point.
- In a strong acid-weak base titration, the pH is less than 7 at the equivalence point.

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7.21: Indicators

"Boil Them Cabbage Down" is an old bluegrass song. Many people enjoy the music, but chemistry students also enjoy the product of boiled cabbage. Extracting the anthocyanin dye from cabbage leaves with boiling water gives a solution that is red when acidic, purple when neutral, and green to yellow when basic.

Indicators

An **acid-base indicator** is a substance that displays different colors when in the presence of an acid or a base. How does that work? An indicator is a weak acid that ionizes within a known pH range, usually about 2 pH units. We can represent the protonated form of the indicator molecule as $\mathbf{HIn}$ and the deprotonated form as $\mathbf{In^-}$. The following equilibrium exists for the indicator:

$$\mathbf{HIn}\,(aq) \rightleftharpoons \mathbf{H^+}\,(aq) + \mathbf{In^-}\,(aq)$$

According to Le Chatelier's principle, the addition of $\mathbf{H^+}$ ions (as in a low pH solution) drives the equilibrium to the left and the protonated $\mathbf{HIn}$ predominates. The addition of $\mathbf{OH^-}$ (as in a high pH solution) decreases the $\mathbf{H^+}$ concentration and drives the equilibrium to the right and the deprotonated $\mathbf{In^-}$ predominates. To be useful as an indicator, the two forms must be different colors. In the case of phenolphthalein, the protonated form is colorless, while the deprotonated form is pink. The figure below shows a variety of acid-base indicators that can be used in titration experiments.

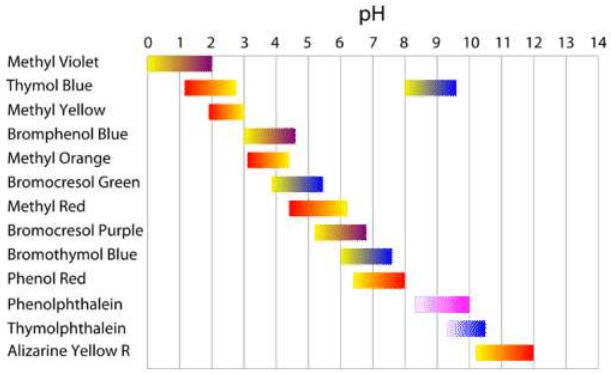


Figure **7.21.1**: pH indicators. (CC BY-NC; CK-12)

Depending on the pH at the equivalence point, the appropriate indicator must be chosen. For example, bromphenol blue has a yellow color below a pH of about 3 and a blue-violet color above a pH of about 4. Bromphenol blue would not be a good choice as the indicator for a strong acid-strong base titration, because the pH is 7 at the equivalence point. Instead, it could be used for a strong acid-weak base titration, where the pH at the equivalence point is lower.

Most indicators have two colored forms. Universal indicator displays the entire rainbow of colors from low pH to high pH (see figure below). Universal indicator is used to make pH paper, which can be used to quickly test solutions for their approximate pH.



Figure **7.21.2**: Universal indicator tape. (CC BY-NC; CK-12)

Summary

- An acid-base indicator is a substance that displays different colors when in the presence of an acid or a base.
- Examples of acid-base indicators are given.

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7.22: Hydrolysis of Salts- Equations

Hydrolysis of Salts: estimation of pH for a salt solution

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions would always be neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$\mathbf{HF\,(aq) + NaOH\,(aq) \rightarrow NaF\,(aq) + H_2O\,(l)} \quad \textbf{(7.22.1)}$$
$$\mathbf{HF\,(aq) + OH^-\,(aq) \rightarrow F^-\,(aq) + H_2O\,(l)} \quad \textbf{(7.22.2)}$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting, to a small extent, with water, accepting a proton.

$$\mathbf{F^-\,(aq) + H_2O\,(l) \rightleftharpoons HF\,(aq) + OH^-\,(aq)} \quad \textbf{(7.22.3)}$$

The fluoride ion is acting as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

The ability of a cation or anion in a salt to undergo hydrolysis, and affect the pH, depends on its strength as an acid or a base, respectively. Only cations that are the conjugate acid of a weak base are strong enough to undergo hydrolysis. This is because a **weak base (low Kb value) will generate a strong conjugate acid (high Ka value)** (remember that K_aK_b=Kw for a conjugate acid-base pair).

Examples for cations:

- Cation generated from a strong base: example Na^+ from NaOH

  NaOH(aq) → Na^+(aq) + HO^-(aq)

strong base (high Kb) weak conjugate acid (low Ka)

Therefore, Na^+ present in a salt cannot react with H_2O. **Na^+ is a neutral cation**:

Na^+(aq) + H_2O(l) → N.R. (no reaction)

- Cation generated from a strong base: example NH_4^+ from NH_3

  NH_3(aq) + H_2O(l) ⇔ NH_4^+(aq) + HO^-(aq)

weak base (low Kb) stronger conjugate acid (high Ka)

Therefore, NH_4^+ present in a salt can react with H_2O in a hydrolysis reaction. **NH_4^+ is an acidic cation:**

NH_4^+(aq) + H_2O(l) ⇔ NH_3(aq) + H_3O^+(aq)

Examples for anions:

- Anion generated from a strong acid: example Cl^- from HCl

  HCl(aq) → Cl-(aq) + H^+(aq)

strong acid (high Ka) weak conjugate base (low Kb)

Therefore, Cl^- present in a salt cannot react with H_2O. **Cl^- is a neutral anion:**

Cl^-(aq) + H_2O(l) → N.R. (no reaction)

- Anion generated from a weak acid: example F- from HF

HF(aq) ⇔ F-(aq) + H^+(aq)

weak acid (low Ka) stronger conjugate base (high Kb)

Therefore, F^- present in a salt can react with H_2O. **F^- is a basic anion:**

F^-(aq) + H_2O(l) ⇔ HF(aq) + OH-(aq)

Estimating the pH of salts

To be able to estimate the pH for a salt, we need to identify the acid-base strength of the cation and the anion in solution, and their ability to undergo hydrolysis with H_2O. **Remember:** only relatively strong conjugate acid and bases can react with water.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved into water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolyzing (NaOH is a strong base), but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ion. That is because F- is the conjugate base of a weak acid (HF), therefore F^- can undergo hydrolysis in water:

$$\mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq) \tag{7.22.4}$$

Salts that are derived from the neutralization of a weak acid (**HF**) by a strong base (**NaOH**) will always produce salt solutions that are basic.

Salts That Form Acidic Solutions

Ammonium chloride (**NH_4Cl**) is a salt that is formed when the strong acid **HCl** is neutralized by the weak base **NH_3**. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolyzing because it is the conjugate base of the strong acid **HCl**. In other words, the **Cl^-** ion cannot accept a proton from water to form **HCl** and **OH^-**, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid. That is because NH_3 is a weak base.

$$\mathrm{NH_4^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_3O^+}\,(aq) + \mathrm{NH_3}\,(aq) \tag{7.22.5}$$

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of **HCl** by **NaOH**. A solution of **NaCl** in water has no acidic or basic properties, since neither ion (Na^+ or Cl^-) is capable of hydrolyzing with H_2O. Other salts that form neutral solutions include potassium nitrate (**KNO_3**) and lithium bromide (**LiBr**). The table below summarizes how to determine the acidity or basicity of a salt solution.

Table 7.22.1

Salt formed from:	Salt Solution	Example
Strong acid + Strong base	Neutral	NaCl
Strong acid + Weak base	Acidic	NH_4Cl
Weak acid + Strong base	Basic	NaF

Salts formed from the reaction of a weak acid and a weak base are more difficult to analyze because competing hydrolysis reactions between the cation and the anion. These salts will not be considered in this concept.

Summary

- Salt hydrolysis is defined.
- Salt hydrolysis reactions resulting in acidic, basic, or neutral solutions are described.

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7.23: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** ($NaC_2H_3O_2$). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (NH_4Cl). Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + C_2H_3O^-_{2(aq)} \tag{7.23.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+_{(aq)} + C_2H_3O^-_{2(aq)} \rightarrow HC_2H_3O_{2(aq)} \tag{7.23.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure **7.23.1** illustrates both actions of a buffer.

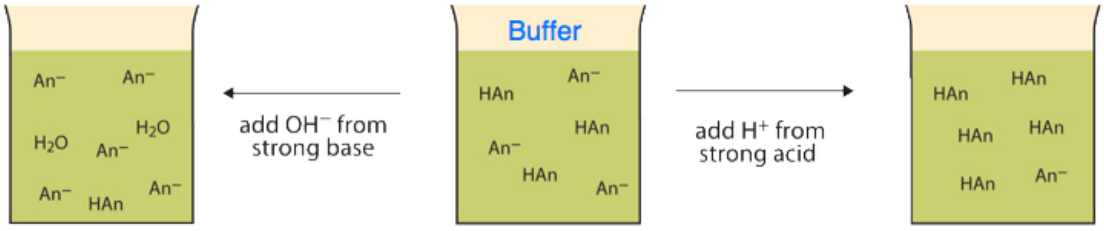


Figure 7.23.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^-. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ *M*) addition of H+ or OH^- that may result from other processes going on in the solution.

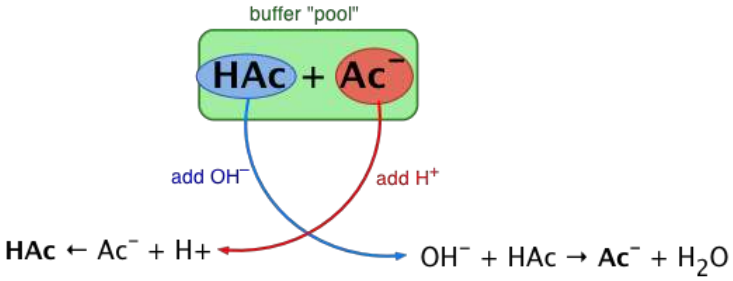


Figure 7.23.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{7.23.3}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{7.23.4}$$

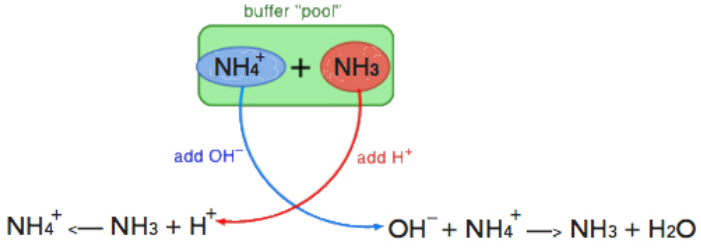


Figure 7.23.3: How NH_4^+/NH_3 buffer works

Example 7.23.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl

c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 7.23.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$ (conjugate base of H_3PO_4) make a buffer.

c. NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

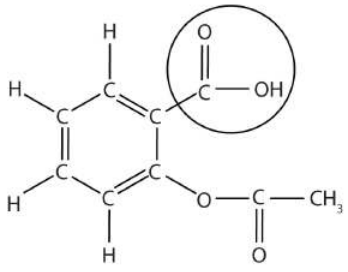


Figure 7.23.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't

formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}\)) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write CO_2(aq)]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathbf{CO_2}(g) + \mathbf{2\,H_2O}(l) \rightleftharpoons \mathbf{H_2CO_3}(aq) \rightleftharpoons \mathbf{HCO_3}^-(aq) + \mathbf{H_3O}^+(aq) \tag{7.23.5}$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathbf{pH} = \mathbf{p}K_\mathbf{a} + \log\frac{[\mathbf{base}]}{[\mathbf{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4 \tag{7.23.6}$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3
    4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.

6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.
3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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7.24: Calculating pH of Buffer Solutions- Henderson-Hasselbalch equation

Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiom

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \tag{7.24.1}$$

Taking negative logarithms of both sides, we obtain

$$-\log [H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \tag{7.24.2}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{7.24.3}$$

Equation 7.24.3 is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

Example 7.24.1: pH of Solution

Find the pH of the solution obtained when 1.00 mol NH_3 and 0.40 mol NH_4Cl are mixed to give 1 L of solution. $K_b(NH_3)$ = 1.8 × 10^{-5} mol L^{-1}.

Solution

In order to use Eq. ???,we need first to have the value of

$$K_a\,(NH_4^+) = \frac{K_w}{K_b\,(NH_3)} \tag{7.24.4}$$

$$= \frac{1.00 \times 10^{-14}\ \text{mol}^2\ \text{L}^2}{1.8 \times 10^{-5}\ \text{mol L}^{-1}} \tag{7.24.5}$$

$$= 5.56 \times 10^{-10}\ \text{mol L}^{-1} \tag{7.24.6}$$

We also have c_a = 0.40 mol L^{-1} and c_b = 1.00 mol L^{-1}. Thus

$$[H_3O^+] = K_a \times \frac{c_a}{c_b} \tag{7.24.7}$$

$$= 5.56 \times 10^{-10}\ \text{mol L}^{-1} \times \frac{0.4\ \text{mol L}^{-1}}{1.0\ \text{mol L}^{-1}} \tag{7.24.8}$$

$$= 2.22 \times 10^{-10}\ \text{mol L}^{-1} \tag{7.24.9}$$

from which

and $\mathbf{pH = 9.65}$

To see why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of acetic acid (3 mol L^{-1})and sodium acetate (2 mol L^{-1}). What would happen if we now added 0.50 mol sodium hydroxide to 1 L of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and acetic acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most will be consumed by reaction with acetic acid. Further, since the hydroxide ion is such a strong base, the reaction

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \tag{7.24.10}$$



will go virtually to completion, and 0.50 mol acetic acid will be consumed. The same amount of acetate ion will be produced. In tabular form:

Species	Initial Concentration mol L^{-1}	Change in Concentration mol L^{-1}	Equilibrium Concentration mol L^{-1}
H_3O^+	2.7 x 10^{-5}	Small	approx. 2.7 x 10^{-5}
CH_3COO^-	2.00	0.50	2.50 + 2.7 x 10^{-5} = 2.50
CH_2COOH	nbsp; 3.00	(-0.50)	2.50 - 2.7 x 10^{-5} = 2.50

Substituting the equilibrium concentrations of base (acetate ion) and conjugate acid (acetic acid) into the Henderson-Hasselbalch equation, Eq. 7.24.3, we have

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{7.24.11}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{(2.50\ \mathrm{mol\ L^{-1}})}{(2.50\ \mathrm{mol\ L^{-1}})} \tag{7.24.12}$$

$$= -(0.25 - 5) + \log(1) \tag{7.24.13}$$

$$= 4.74 + 0 = 4.74 \tag{7.24.14}$$

The addition of 0.5 mol sodium hydroxide to buffer mixture has thus succeeded in raising its pH from 4.57 to only 4.74. If the same 0.5 mol had been added to a cubic decimeter of pure water, the pH would have jumped all the way from 7.00 up to 13.7! The buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of

$$\frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]} \tag{7.24.15}$$

As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by

$$[\mathrm{H_3O^+}] = K_a\frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]} \tag{7.24.16}$$

the hydronium-ion concentration and pH are also altered to only a small extent.

The ability of a buffer solution to resist large changes in pH has a great many chemical applications, but perhaps the most obvious examples of buffer action are to be found in living matter. If the pH of human blood, for instance, gets outside the range 7.2 to 7.6, the results are usually fatal. The pH of blood is controlled by the buffering action of several conjugate acid-base pairs. The most important of these is undoubtedly the H_2CO_3/HCO_3^- pair, but side chains of the amino acid histidine in the hemoglobin molecule also play a part. (Hemoglobin, a protein, is the red substance in the blood. It is responsible for carrying oxygen away from the lungs.) Most enzymes (biological catalysts) can only function inside a rather limited pH range and must therefore operate in a buffered environment. The enzymes which start the process of digestion in the mouth at a pH of around 7 become inoperative in the stomach at a pH of 1.4. The stomach enzymes in turn cannot function in the slightly basic environment of the intestines.

Contributors

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CHAPTER OVERVIEW

8: Radioactivity and Nuclear Processes

8.1: Nuclear Radiation
8.2: Half-Life
8.3: Effects of Radiation
8.4: Units of Radioactivity
8.5: Uses of Radioactive Isotopes
8.6: Nuclear Fission
8.7: Nuclear Fusion
8.8: Nuclear Energy

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8.1: Nuclear Radiation

Learning Outcomes

- Define radioactivity.
- Describe a radioisotope.
- Explain how radioactivity involves a change in the nucleus of a radioisotope.
- Explain the characteristics of the forms of radiation.
- Describe and write equations for the primary types of radioactive decay.

Marie Curie (1867 - 1934) was a Polish scientist who pioneered research into nuclear radiation (Figure **8.1.1**). She was awarded the Nobel Prize in physics in 1903 along with her husband Pierre and Antoine Henri Becquerel for their work on radioactivity. She was awarded a second Nobel Prize in 1911, this time in chemistry, for her continued research on radioactive elements. In this lesson, you will learn about radioactivity, the reasons why certain elements and isotopes are radioactive, and the most common types of radioactive decay processes.



Figure **8.1.1**: Marie Curie was one of the leading scientists in the field of radioactivity. She discovered two radioactive elements and was awarded two Nobel Prizes for her work.

Radioactivity

Radioactivity was discovered quite by accident. In 1896, Henri Becquerel was studying the effect of certain uranium salts on photographic film plates. He believed that the salts had an effect on the film only when they had been exposed to sunlight. He accidentally found that uranium salts that had not been exposed to sunlight still had an effect on the photographic plates. The Curies, associates of Becquerel at the time, showed that the uranium was emitting a type of ray that interacted with the film. Marie Curie called this radioactivity. **Radioactivity** *is the spontaneous breakdown of an atom's nucleus by the emission of particles and/or radiation*. **Radiation** *is the emission of energy through space in the form of particles and/or waves*.

Nuclear reactions are very different from chemical reactions. In chemical reactions, atoms become more stable by participating in a transfer of electrons or by sharing electrons with other atoms. In nuclear reactions, it is the nucleus of the atom that gains stability by undergoing a change of some kind. Some elements have no stable isotopes, which means that any atom of that element is radioactive. For some other elements, only certain isotopes are radioactive. A **radioisotope** *is an isotope of an element that is unstable and undergoes radioactive decay*. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

The discovery of radioactivity and its effects on the nuclei of elements disproved Dalton's assumption that atoms are indivisible. A **nuclide** *is a term for an atom with a specific number of protons and neutrons in its nucleus*. As we will see, when nuclides of one type emit radiation, they are changed into different nuclides. Radioactive decay is spontaneous and does not required an input of energy to occur. The stability of a particular nuclide depends on the composition of its nucleus, including the number of protons, the number of neutrons, and the proton-to-neutron ratio.

The Band of Stability

Carbon-12, with six protons and six neutrons, is a stable nucleus, meaning that it does not spontaneously emit radioactivity. Carbon-14, with six protons and eight neutrons, is unstable and naturally radioactive. Among atoms with lower atomic numbers, the ideal ratio of neutrons to protons is approximately 1:1. As the atomic number increases, the stable neutron-proton ratio

gradually increases to about 1.5:1 for the heaviest known elements. For example, lead-206 is a stable nucleus that contains 124 neutrons and 82 protons, a ratio of 1.51 to 1.

This observation is shown in the figure below. The **band of stability** *is the range of stable nuclei on a graph that plots the number of neutrons in a nuclide against the number of protons.* Known stable nuclides are shown with individual blue dots, while the 1:1 and 1.5:1 ratios are shown with a solid red line and a green line, respectively.

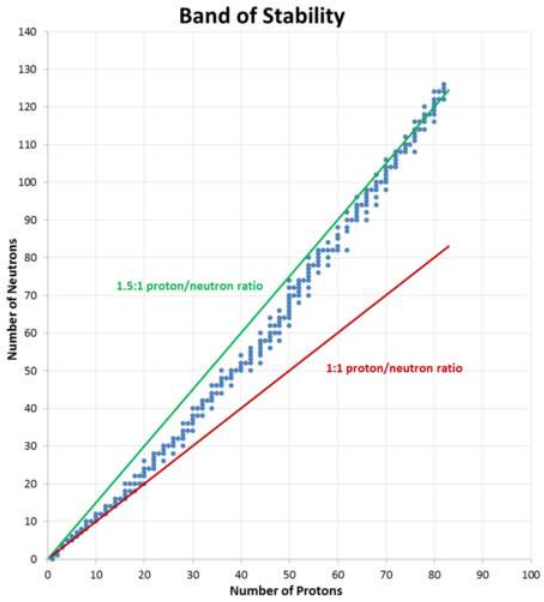


Figure 8.1.2: A graph of the number of neutrons in a nucleus as a function of the number of protons. Each known stable nucleus is represented by a blue dot. The ideal neutron to proton ratio changes from 1:1 for light nuclei to 1.5:1 for the heaviest nuclei.

It should be noted that just because a nucleus is "unstable" (able to undergo spontaneous radioactive decay) does not mean that it will rapidly decompose. For example, uranium-238 is unstable because it spontaneously decays over time, but if a sample of uranium-238 is allowed to sit for 1000 years, only 0.0000155% of the sample will have decayed. However, other unstable nuclei, such as berkelium-243, will be almost completely gone ($>99.9999\%$ decayed) in less than a day.

Radioactive Decay

Unstable nuclei spontaneously emit radiation in the form of particles and energy. This generally changes the number of protons and/or neutrons in the nucleus, resulting in a more stable nuclide. A **nuclear reaction** *is a reaction that affects the nucleus of an atom.* One type of a nuclear reaction is **radioactive decay**, *a reaction in which a nucleus spontaneously disintegrates into a slightly lighter nucleus, accompanied by the emission of particles, energy, or both.* An example is shown below, in which the nucleus of a polonium atom radioactively decays into a lead nucleus.

$$^{210}_{84}\text{Po} \rightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He} \tag{8.1.1}$$

Note that in a balanced nuclear equation, the sum of the atomic numbers (subscripts) and the sum of the mass numbers (superscripts) must be equal on both sides of the equation. Recall the notation system for isotopes, which shows both the atomic number and mass number along with the chemical symbol.



Because the number of protons changes as a result of this nuclear reaction, the identity of the element changes. **Transmutation** *is a change in the identity of a nucleus as a result of a change in the number of protons.* There are several different types of naturally occurring radioactive decay, and we will examine each separately.

Alpha Decay

An **alpha particle** (α) *is a helium nucleus with two protons and two neutrons.* Alpha particles are emitted during some types of radioactive decay. The net charge of an alpha particle is $2+$, and its mass is approximately $4\ \text{amu}$. The symbol for an alpha particle

in a nuclear equation is usually ^4_2He, though sometimes α is used. Alpha decay typically occurs for very heavy nuclei in which the nuclei are unstable due to large numbers of nucleons. For nuclei that undergo alpha decay, their stability is increased by the subtraction of two protons and two neutrons. For example, uranium-238 decays into thorium-234 by the emission of an alpha particle (see figure below).

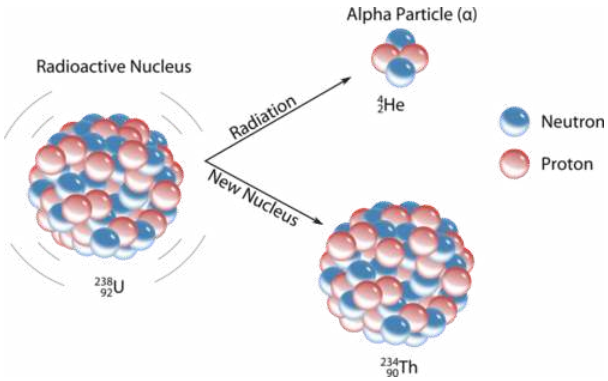


Figure 8.1.3: The unstable uranium-238 nucleus spontaneously decays into a thorium-234 nucleus by emitting an alpha particle.

Beta Decay

Nuclei above the band of stability are unstable because their neutron to proton ratio is too high. To decrease that ratio, a neutron in the nucleus is capable of turning into a proton and an electron. The electron is immediately ejected at a high speed from the nucleus. A **beta particle** (β) *is a high-speed electron emitted from the nucleus of an atom during some kinds of radioactive decay* (see figure below). The symbol for a beta particle in an equation is either β or $^0_{-1}\text{e}$. Carbon-14 undergoes beta decay, transmutating into a nitrogen-14 nucleus.

$$^{14}_6\text{C} \rightarrow {}^{14}_7\text{N} + {}^0_{-1}\text{e} \tag{8.1.2}$$

Note that beta decay increases the atomic number by one, but the mass number remains the same.

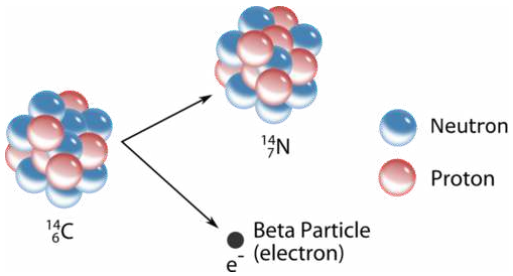


Figure 8.1.4: The beta decay of a carbon-14 nuclide involves the conversion of a neutron to a proton and an electron, with the electron being emitted from the nucleus.

Positron Emission

Nuclei below the band of stability are unstable because their neutron to proton ratio is too low. One way to increase that ratio is for a proton in the nucleus to turn into a neutron and another particle called a positron. A **positron** *is a particle with the same mass as an electron, but with a positive charge*. Like the beta particle, a positron is immediately ejected from the nucleus upon its formation. The symbol for a positron in an equation is $^0_{+1}\text{e}$. For example, potassium-38 emits a positron, becoming argon-38.

$$^{38}_{19}\text{K} \rightarrow {}^{38}_{18}\text{Ar} + {}^0_1\text{e} \tag{8.1.3}$$

Positron emission decreases the atomic number by one, but the mass number remains the same.

Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called electron capture. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\mathrm{Ag} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{106}_{46}\mathrm{Pd} \tag{8.1.4}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Gamma Ray Emission

Gamma rays (γ) *are very high energy electromagnetic waves emitted from a nucleus.* Gamma rays are emitted by a nucleus when nuclear particles undergo transitions between nuclear energy levels. This is analogous to the electromagnetic radiation emitted when excited electrons drop from higher to lower energy levels; the only difference is that nuclear transitions release much more energetic radiation. Gamma ray emission often accompanies the decay of a nuclide by other means.

$$^{230}_{90}\mathrm{Th} \rightarrow {}^{226}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He} + \gamma \tag{8.1.5}$$

The emission of gamma radiation has no effect on the atomic number or mass number of the products, but it reduces their energy.

Summary of Nuclear Radiation

The table below summarizes the main types of nuclear radiation, including charge, mass, symbol, and penetrating power. Penetrating power refers to the relative ability of the radiation to pass through common materials. Radiation with high penetrating power is potentially more dangerous because it can pass through skin and do cellular damage.

Table **8.1.1** *Summary of types of nuclear radiation.*

Type	Symbol	Mass number	Charge	Penetration Power	Shielding
Alpha particle	$^{4}_{2}\mathrm{He}$ or α	4	2+	Low	Paper, skin
Beta particle	$^{0}_{-1}\mathrm{e}$ or β	0	1−	Moderate	Heavy cloth, plastic
Positron	$^{0}_{1}\mathrm{e}$ or β^{+}	0	1+	Moderate	Heavy cloth, plastic
Gamma ray	γ or $^{0}_{0}\gamma$	0	0	High	Lead, concrete
Neutron	$^{1}_{0}\mathrm{n}$	1	0	High	Water, lead

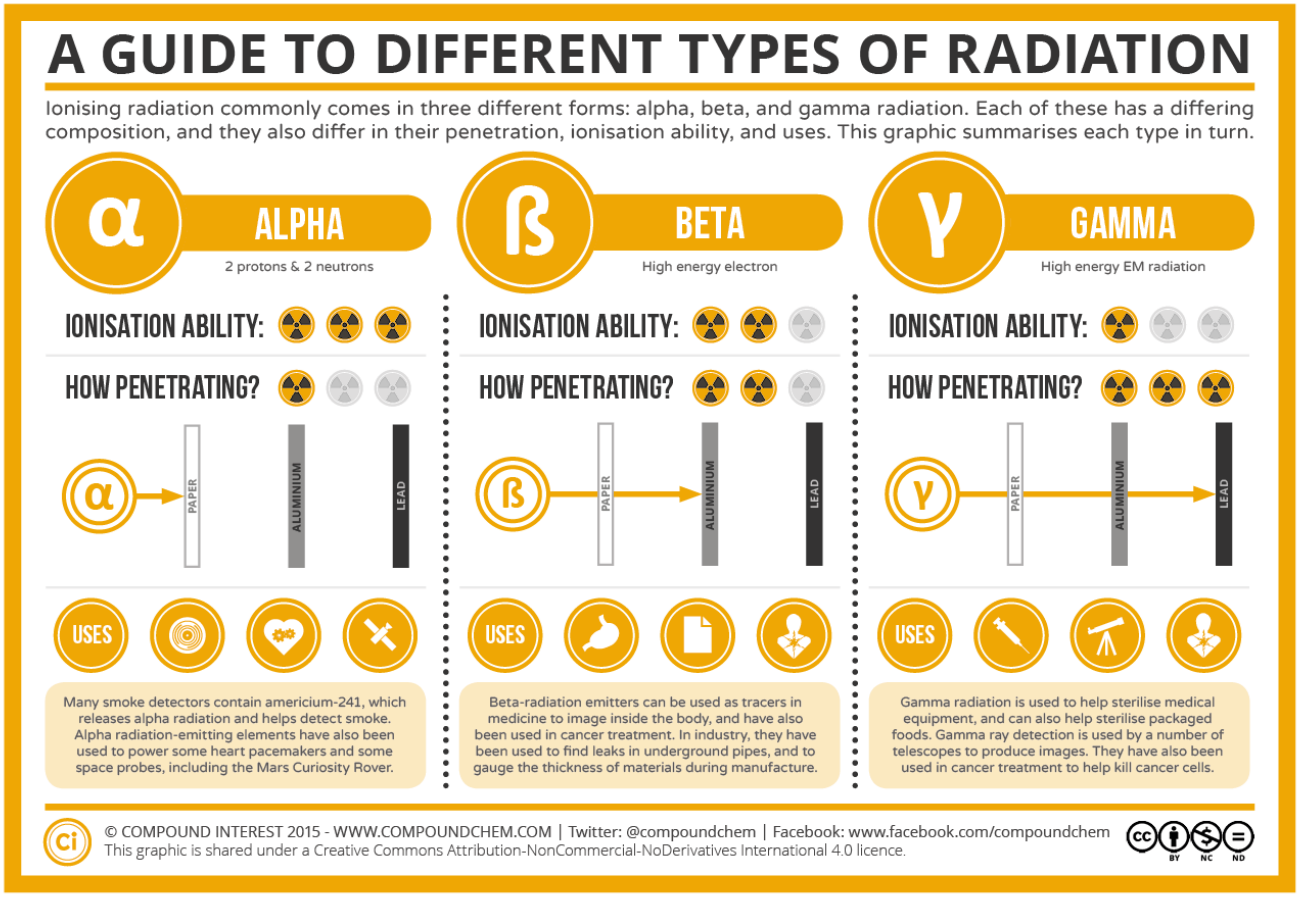


Figure **8.1.5**: Infographic showing the different properties of radiation. "A Guide to Different Types of Radiation" is by Compound Interest is licensed under CC BY NC ND 4.0.

Supplemental Resources

- Atomic structure review: www.sciencegeek.net/Chemistry...t1Numbers2.htm
- Balancing Nuclear equations: www.sciencegeek.net/Chemistry...rEquations.htm
- Nuclear decay: www.sciencegeek.net/Chemistry...cleardecay.htm

Contributors and Attributions

-
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8.2: Half-Life

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**, which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of tritium (a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed from hydrogen-3 to helium-3 by emitting a beta particle, so that only 50.0 g of the original tritium remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining tritium will have decayed, leaving 25.0 g of tritium. After another 12.3 y—now a total of 36.9 y—another half of the remaining tritium will have decayed, leaving 12.5 g. This sequence of events is illustrated in Figure 8.2.1 - Radioactive Decay.

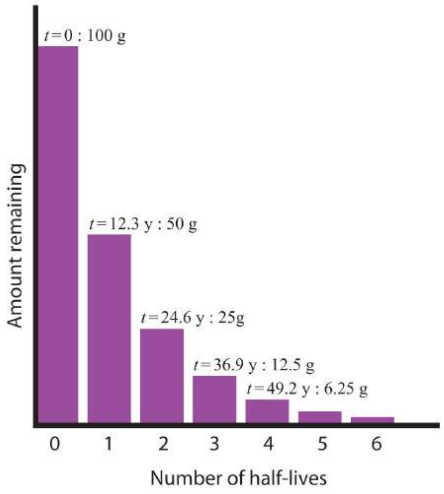


Figure **8.2.1** Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\textbf{amount remaining} = \textbf{initial amount} \times \left(\frac{1}{2}\right)^{n}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 8.2.1

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so we use the previous expression n = 4. Substituting and solving results in the following:

$$\begin{aligned}\textbf{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

Exercise 8.2.1

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table **8.2.1** - Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table **8.2.1** Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. The following table summarizes radioactivity in the normal human body.

Table with four columns and eight rows. The first column on the left is labeled as Radioactive Isotope, underneath in the rows has radioactive isotopes. The second column is labeled as Half-Life (y), underneath in the rows has half-lives. The third column is labeled as Isotope Mass in the Body (g), underneath in the rows has isotope masses. The fourth column on right is labeled as Activity in the Body (decays/s), underneath in the rows has the activities in the body as the decays.

Radioactive Isotope	Half-Life (y)	Isotope Mass in the Body (g)	Activity in the Body (decays/s)
^{40}K	1.26×10^{9}	0.0164	4,340
^{14}C	5,730	1.6×10^{-8}	3,080
^{87}Rb	4.9×10^{10}	0.19	600
^{210}Pb	22.3	5.4×10^{-10}	15
^{3}H	12.3	2×10^{-14}	7
^{238}U	4.47×10^{9}	1×10^{-4}	5
^{228}Ra	5.76	4.6×10^{-14}	5
^{226}Ra	1,620	3.6×10^{-11}	3

The average human body experiences about 8,000 radioactive decays.

Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

What if the elapsed time is not an exact number of half-lives? We can still calculate the amount of material we have left, but the equation is more complicated. The equation is

$$\text{amount remaining} = (\text{amount initial}) \times e^{-0.693t/t_{1/2}}$$

where e is the base of natural logarithms (2.71828182…), t is the elapsed time, and $t_{1/2}$ is the half-life of the radioactive isotope. The variables t and $t_{1/2}$ should have the same units of time, and you may need to make sure you know how to evaluate natural-logarithm powers on your calculator (for many calculators, there is an "inverse logarithm" function that you can use; consult your instructor if you are not sure how to use your calculator). Although this is a more complicated formula, the length of time t need not be an exact multiple of half-lives.

Example 8.2.2

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 60.0 s?

Solution

Although similar to Example 3, the amount of time is not an exact multiple of a half-life. Here we identify the initial amount as 5.00 g, t = 60.0 s, and $t_{1/2}$ = 11.0 s. Substituting into the equation:

$$\text{amount remaining} = (5.00\text{ g}) \times e^{-(0.693)(60.0\text{ s})/11.0\text{ s}}$$

Evaluating the exponent (and noting that the s units cancel), we get

$$\text{amount remaining} = (5.00\text{ g}) \times e^{-3.78}$$

Solving, the amount remaining is 0.114 g. (You may want to verify this answer to confirm that you are using your calculator properly.)

? Exercise 8.2.2

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 100.0 y?

Answer

0.189 g

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

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8.3: Effects of Radiation

Bacterial contamination in our food often makes the news. There are many bacteria present on raw food, especially raw meat. Campylobacter, salmonella, and other microorganisms can be present, even after cooking, if the meat has not been sufficiently exposed to the heat. Ionizing radiation can be used to disrupt the DNA-RNA-protein synthesis cycle that allows the bacteria to reproduce. Cobalt-60 is a common radiation source, as is cesium-137. But...just to be safe...order that burger well-done!

Effects of Radiation

In order to better understand how cellular radiation damage occurs, we need to take a quick review of how the cell functions. **DNA** in the nucleus is responsible for protein synthesis and for regulation of many cellular functions. In the process of protein synthesis, DNA partially unfolds to produce **messenger RNA** (mRNA). The mRNA leaves the nucleus and interacts with ribosomes, transfer RNA, amino acids, and other cellular constituents in the cytoplasm. Through a complex series of reactions, proteins are produced to carry out a number of specialized processes within the organism. Anything that disturbs this flow of reactions can produce damage to the cell.

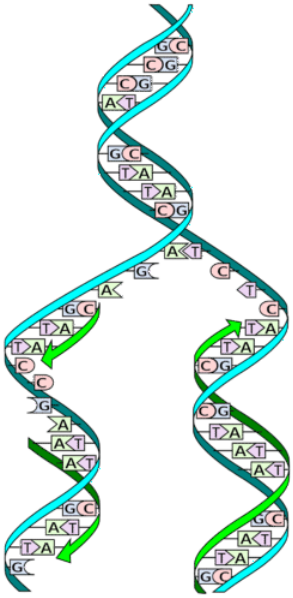


Figure **8.3.1**: DNA replication.

The major effect of ionizing radiation on the cell is the disruption of the DNA strand. With the DNA structure damaged, the cell cannot reproduce in its normal fashion. Protein synthesis is affected, as are a number of processes necessary for proper cell function. One common effect is the generation of cancer cells. These cells have an abnormal structure due to the damaged DNA. In addition, they usually grow rapidly since the normal control processes regulating cell growth have been changed by the altered composition of the DNA. Tissue damage is also common in people with severe exposure to radiation.

Effects of Radiation on Humans

We can see two general types of effects when humans are exposed to radiation. Low-level exposure can lead to development of cancer. The regulatory processes regulating cell growth are disrupted, leading to uncontrolled growth of abnormal cells. Acute exposure can produce nausea, weakness, skin burns, and internal tissue damage. Cancer patients receiving radiation therapy experience these symptoms; the radiation is targeted to a specific site in the body so that the damage is primarily to the cancer cells, and the patient is able to recover from the exposure.

Summary

- Anything that affects DNA replication and protein synthesis can damage a cell.
- Effects of ionizing radiation on protein synthesis are listed.
- The impact of ionizing radiation on human health is discussed.

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8.4: Units of Radioactivity

Learning Objective

- Express amounts of radioactivity in a variety of units.

In Section 15.2, we used mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one **becquerel (Bq).** Even in a small mass of radioactive material, however, there are thousands upon thousands of decays or disintegrations per second. The unit **curie (Ci)**, now defined as 3.7×10^{10} decays/s, was originally defined as the number of decays per second in 1 g of radium. Many radioactive samples have activities that are on the order of microcuries (μCi) or more. Both the becquerel and the curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi. (The curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena in the early 1900s; the becquerel is named after Henri Becquerel, who discovered radioactivity in 1896.)

Example 8.4.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

Solution

The following table shows the activity of the radium sample over multiple half-lives:

Solutions to Example 15.4.1

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus it takes 4 half-lives, or 4 × 1,600 y = 6,400 y, for the activity to decrease to 1.0 mCi.

Exercise 8.4.1

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Answer

60 h

Example 8.4.2

A sample of radium has an activity of 16.0 mCi. If the half-life of radium is 1,600 y, how long before the sample's activity is 5.6 mCi?

Solution

In this case we do not have an exact number of half-lives, so we need to use the more complicated equation (Section 15.2) and solve for time. If the initial amount is represented by 16.0 mCi and the final amount is 5.6 mCi, we have

$$5.6\,mCi = (16.0\,mCi)e^{-0.693t/(1{,}600\,y)}$$

To solve, we divide both sides of the equation by 16.0 mCi to cancel the millicurie units:

$$\frac{5.6}{16.0} = e^{-0.693t/(1{,}600y)}$$

By taking the natural logarithm of both sides; the natural logarithm cancels the exponential function. The natural logarithm of 5.6/16.0 is −1.050. So

$$-1.050 = \frac{-0.692t}{1{,}600\,y}$$

The negative sign cancels, and we solve for t. Thus

$$t = 2{,}420\,y$$

It makes sense that the time is greater than one half-life (1,600 y) because we have less than one-half of the original activity left.

Exercise 8.4.2

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 10,000 Bq?

Answer

38.8 h

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue, and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, like the thermal energy from boiling water, the transferred energy can damage the tissue.

The **rad** (an acronym for radiation absorbed dose) is a unit equivalent to 1 g of tissue absorbing 0.01 J:

$$1\ \text{rad} = 0.01\ \text{J/g}$$

Another unit of radiation absorption is the gray (Gy):

$$1\ \text{Gy} = 100\ \text{rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of water (approximately the same mass as a 150 lb person) would increase the temperature of the water by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that different types of emissions affect various tissues differently. To quantify these effects, the unit **rem** (an acronym for *röntgen equivalent man*) is defined

$$\text{asrem} = \text{rad} \times \text{factor}$$

where factor is a number greater than or equal to 1, that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, the factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye

tissue the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X-ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table **8.4.1**, lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources—sources we cannot avoid. Fully 10% of the exposure comes from our own bodies, largely from carbon-14 and potassium-40.

Table **8.4.1**: Average Annual Radiation Exposure (Approximate)

Source	Amount (mrem)
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28*
consumer products	10
nuclear energy	0.05
Total	358
*Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from cosmic radiation.	

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table **8.4.2** - Effects of Short-Term Exposure to Radioactivity and Radiation, lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Table **8.4.2**: Effects of Short-Term Exposure to Radioactivity and Radiation

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible "burns" in skin, nausea, vomiting, fatigue
>300	loss of white blood cells; hair loss
~600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. Comparing the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.

Another means of detecting radioactivity is an electrical device called a **Geiger counter** (Figure **8.4.1**). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter.

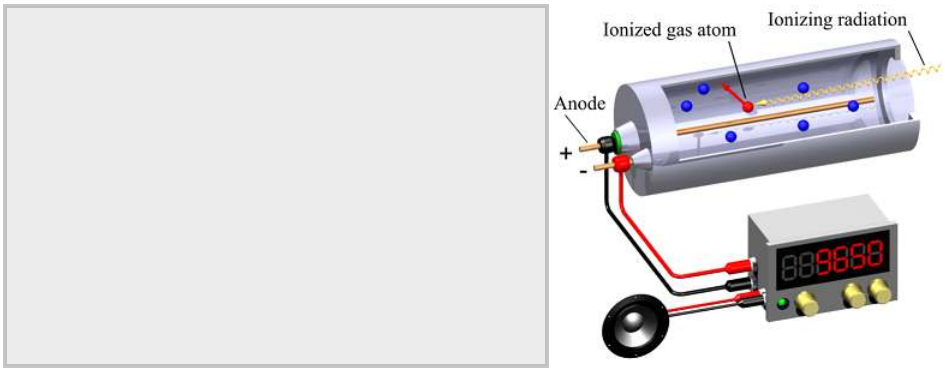


Figure 8.4.2: (left) Geiger counter with pancake type probe. Public Domain; TimVickers via Wikipedia. (right) Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia).

Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter.

0:00 / 0:00

Key Takeaway

- Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

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8.5: Uses of Radioactive Isotopes

Learning Objective

- Learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful because either we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A **tracer** is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of carbon-14 to determine the steps involved in photosynthesis in plants. We know these steps because researchers followed the progress of carbon-14 throughout the process.

Radioactive Dating

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about $4.5 \times 10^9 y$. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over $4 \times 10^9 y$.

In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope, carbon-14, is particularly useful in determining the age of once-living artifacts. A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, albeit very low, level. Once a living thing dies, it no longer acquires carbon-14; as time passes the carbon-14 that was in the tissues decays. (The half-life of carbon-14 is 5,370 y.) If a once-living artifact is discovered and analyzed many years after its death and the remaining carbon-14 is compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (Figure **8.5.1** purported by some to be the burial cloth of Jesus Christ and composed of flax fibers, a type of plant) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

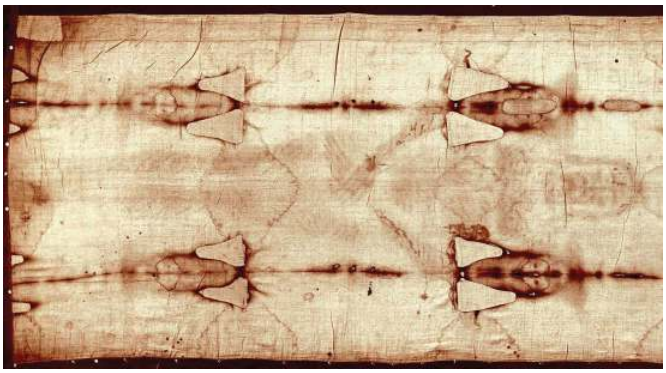


Figure **8.5.1**: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

Irradiation of Food

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, extending the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Medical Applications

Radioactive isotopes have numerous medical applications in diagnosing and treating illness and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure **8.5.1**). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of ^{131}I is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

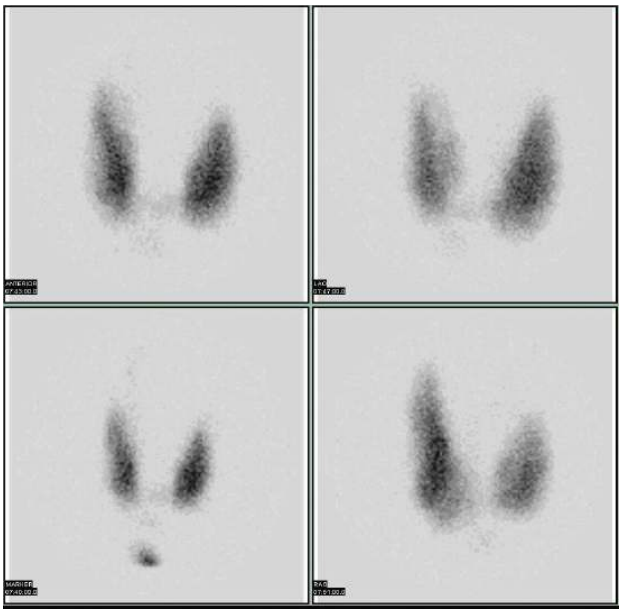


Figure **8.5.2**: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, en.Wikipedia.org/wiki/File:Thyroid_scan.jpg.

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor were detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less than 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect, but also to ease the pain of bone cancers. Table **8.5.1** lists several radioactive isotopes and their medical uses.

Table **8.5.1**: Some Radioactive Isotopes with Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumors
$^{99m}Tc^{*}$	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis

*The "m" means that it is a metastable form of this isotope of technetium.

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

Food and Drink Application: Radioactivity in Wines

Wine lovers put some stock in *vintages*, or the years in which the wine grapes were grown before they were turned into wine. Wine can differ in quality depending on the vintage. Some wine lovers willingly pay much more for a bottle of wine with a certain vintage. But how does one verify that a bottle of wine was in fact part of a certain vintage? Is the label a fake? Is that stash of wine found in the basement of a French chateau really from the 1940s, or was it made in 2009?

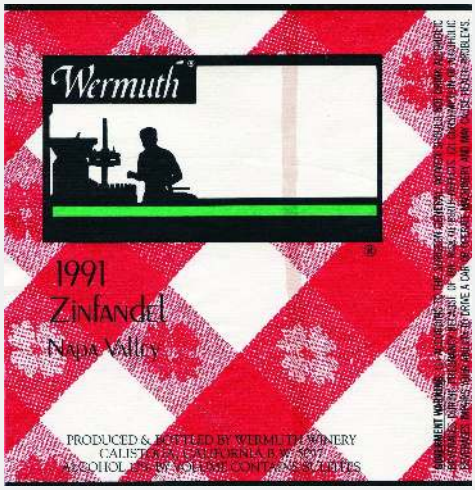


Figure **8.5.3**: A wine label. This wine label from a bottle of wine claims a vintage of 1991. Is the wine really from this vintage, or is it a fake? Radioactivity can help determine the answer. Source: Used by permission of Ralph E. Wermuth.

Cesium-137 is a radioactive isotope that has a half-life of 30.1 y. It was introduced into the atmosphere in the 1940s and 1950s by the atmospheric testing of nuclear weapons by several countries after World War II. A significant amount of cesium-137 was released during the Chernobyl nuclear disaster in 1986. As a result of this atmospheric contamination, scientists have precise measurements of the amount of cesium-137 available in the environment since 1950. Some of the isotope of cesium is taken up by living plants, including grape vines. Using known vintages, oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the passage of time, researchers can collect evidence for or against a claimed wine vintage.

> Before about 1950, the amount of cesium-137 in the environment was negligible, so if a wine dated before 1950 shows any measurable cesium-137 activity, it is almost surely a fake, so do not shell out lots of money for it! It may be a good wine, but it is almost definitely not over 60 years old.

Summary

Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and preservation of food.

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8.6: Nuclear Fission

The process by which nitrogen is converted to carbon-14 is an example of *neutron capture*, in which particles are absorbed by the nucleus of another atom to form a new element. These types of reactions are actually quite common in nuclear chemistry. A uranium-235 nucleus captures a “slow-moving” neutron, just like nitrogen captures a neutron, leading to the formation of carbon-14. Initially, uranium-236 is formed, but this nucleus has a neutron-to-proton ratio that makes it exceptionally unstable. The unstable nucleus instantaneously breaks apart (undergoes **fission**) to form lighter elements and to release additional free neutrons. As the nucleus breaks apart, a significant amount of energy is also released. A nuclear equation showing a typical fission of uranium-235 is shown below:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3^{1}_{0}n$$

The three neutrons that are released are now speeding through the mass of uranium. If these are captured by another nucleus, the process happens again and three more neutrons are released. This represents a *chain reaction*, and in order to sustain a chain reaction like this, the mass or uranium must be large enough so that the probability of every released neutron being captured by another uranium is high. The mass of uranium (or other fissile element) that is required in order to sustain a chain reaction is called the **critical mass**.

The process of nuclear fission is best known within the context of fission bombs and as the process that operates within nuclear power plants. Designing a workable fission bomb presents many technical challenges. A mass of fissile material that exceeds the critical mass is unstable, so you must begin with a smaller, non-critical mass and somehow create one within a few microseconds. In the original design, this was accomplished by taking two non-critical pieces and forcing them together (very rapidly). This is typically referred to as a “gun assembly”, in which one piece of fissile uranium is fired at a fissile uranium target at the end of the weapon, similar to firing a bullet down a gun barrel.

Each of the uranium fragments are less than a critical mass, but when they collide, they form a mass capable of sustaining the nuclear chain reaction. The assembly stays together for a few microseconds before the energy released from the fission blows it to pieces. The trick is designing nuclear devices like this is to keep them together long enough so that enough energy is released. Neutron reflectors and “boosters” are generally used to accomplish this, nonetheless, this basic type of weapon is inefficient, although easy to design and incredibly deadly. A critical mass of uranium-235 is a sphere that is slightly less than 7 inches in diameter.

A much more efficient fission bomb is based on achieving a critical mass of fissile material, not by combining smaller fragments, but by increasing the density of a sub-critical mass to the point that the rate of neutron capture sustains the chain reaction. This design is called the “implosion” bomb and it basically consists of a sphere of fissile material surrounded by shaped explosives that must be detonated simultaneously. The resulting shock wave compresses the fissile material, allowing the chain reaction to occur. This type of design requires much less fissile material, but is technically challenging. Modern devices have neutron reflectors, “neutron initiators”, etc., and sophisticated bombs can be efficient, have a high yield and a relatively small physical size.

In a nuclear reactor designed to heat water, produce steam and electrical power, the chemistry is the same, but *control rods* are introduced between the pieces of fissile material to absorb some of the neutrons that are produced so that a critical mass is never achieved and the chain reaction can be controlled. In this set-up, as the control rods are withdrawn, the chain reaction speeds up, and as they are inserted, the reaction slows down. Even under “meltdown” conditions, where control rods fail, the critical mass of fissile material would be formed slowly. The resulting explosion would be a bad thing, but would not compare with the energy released from a well-designed fission weapon.

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8.7: Nuclear Fusion

As we saw in the preceding section, when the nuclei of heavy atoms split, energy is released. For light atoms, the opposite is true; when these nuclei combine (fuse together), energy is released. This is the process of nuclear fusion. Fusion of light elements, mostly hydrogen, is the force that powers energy release in the sun and in sun-like stars. Imagine the sun as a huge sphere of hydrogen. Because a star is so massive, the gravitation pull on the hydrogen atoms is sufficient to overcome the repulsion between the two nuclei to force them together to form an unstable ${}^{2}_{2}\mathrm{He}$ nucleus. This immediately ejects a positron, leaving deuterium, ${}^{2}_{1}\mathrm{H}$, and releasing a significant amount of energy. In the cascade of reactions deuterium fuses with another hydrogen to give ${}^{3}_{2}\mathrm{He}$, and two of these combine to form helium, ejecting two high-energy protons in the process.

In stars that are larger and heavier than our sun, the “triple alpha process” is the dominant nuclear reaction. In this, helium nuclei fuse to eventually form carbon, releasing significant energy in the process.

One of the great challenges in physics and engineering today is to replicate fusion of this sort under controlled conditions, harvesting the energy released and converting it, indirectly, into electrical power. The extremely high temperatures and pressures that are required to initiate and sustain fusion reactions thwarted, thus far, attempts to build a fusion reactor that is “break even” in terms of the energy released relative to the energy required to produce the fusion events. Uncontrolled fusion is certainly possible, and fusion bombs exist, but these typically use an advanced fission bomb to create the temperatures and pressures necessary to promote the fusion of the lighter elements. Clearly, this approach does not work in the laboratory! Work on fusion reactors continues at a fast pace and includes novel approaches such as *aneutronic* fusion reactions that utilize proton-boron fusion to produce charged particles rather than a barrage of neutrons. The advantage here is that few neutrons are produced, reducing the need for shielding, and the charged particles formed can potentially be captured *directly* as electricity.

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8.8: Nuclear Energy

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear equation, in which the molar mass of each species is indicated to four decimal places:

$$^{235}_{235.0439}\mathrm{U} \rightarrow ^{139}_{138.9088}\mathrm{Ba} + ^{94}_{93.9343}\mathrm{Kr} + ^{2^1}_{2\times1.0087}\mathrm{n}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum=234.8605) we notice a mass difference of -0.1834 g or -0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (E) and mass (m) are related by the following equation:

$$E = mc^2$$

where c is the speed of light, or

$$c = 3.00 \times 10^8\, m/s$$

In the course of the chemical reaction for uranium, the mass difference is converted to energy, which is given off by the reaction:

$$E = (-0.0001834\, kg)(3.00 \times 10^8\, m/s)^2 = -1.65 \times 10^{13} J = -1.65 \times 10^{10} kJ$$

(For the units to work out, mass must be expressed in units of kilograms.) That is, 16.5 billion kJ of energy is given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650kJ/mol of energy for every CH_2 unit in the hydrocarbon, on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. **Nuclear energy** involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$$^{235}\mathrm{U} + \mathrm{mtd} + +3^1$$

Thus by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes. (Artificial or induced radioactivity, in which neutrons are injected into a sample of matter that subsequently cause fission, was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.)

Plutonium-239 can absorb a neutron and undergo a fission reaction to make an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Solution

Using the data given, we can write the following initial equation:

$$^1_0\mathrm{n} + ^{239}_{94}\mathrm{Pu} \rightarrow ^{204}_{79}\mathrm{Au} + ^{31}_{15}\mathrm{P} + ?^1_0\mathrm{n}$$

In balanced nuclear equations, the sums of the subscripts on each side of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced:

0 + 94 = 94 and 79 + 15 = 94.

The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus the balanced nuclear equation is as follows:

$$^{1}_{0}\text{n} + {}^{239}_{94}\text{Pu} \rightarrow {}^{204}_{79}\text{Au} + {}^{31}_{15}\text{P} + 5{}^{1}_{0}\text{n}$$

We predict that the overall process will give off five neutrons.

? Exercise 8.8.1

Uranium-238 can absorb a neutron and undergo a fission reaction to produce an atom of cesium-135 and an atom of rubidium-96. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Answer

$$^{1}_{0}\text{n} + {}^{238}_{92}\text{U} \rightarrow {}^{96}_{37}\text{Rb} + {}^{135}_{55}\text{Cs} + 8{}^{1}_{0}\text{n}$$

eight neutrons

One balanced nuclear reaction for the fission of plutonium-239 is as follows:

$$\underset{1.0087}{^{1}_{0}\text{n}} + \underset{239.0522}{^{239}_{94}\text{Pu}} \rightarrow \underset{203.9777}{^{204}_{79}\text{Au}} + \underset{30.9738}{^{31}_{15}\text{P}} + \underset{5\times1.0087}{5{}^{1}_{0}\text{n}}$$

The molar mass in grams of each species is given for each particle. What is the energy change of this fission reaction?

Solution

We start by adding the masses of all species on each side of the nuclear equation. Then we determine the difference in mass as the reaction proceeds and convert this to an equivalent amount of energy. The total mass of the reactants is as follows:

1.0087 + 239.0522 = 240.0609 g

The total mass of the products is as follows:

203.9777 + 30.9738 + (5 × 1.0087) = 239.9950 g

The change is mass is determined by subtracting the mass of the reactants from the mass of the products:

change in mass = 239.9950 − 240.0609 = −0.0659 g

This mass change must be converted into kilogram units:

$$-0.0659g \times \frac{1kg}{1,000g} = -0.0000659kg$$

Now we can use Einstein's equation to determine the energy change of the nuclear reaction:

E = (−0.0000659 kg)(3.00 × 10^{8} m/s)^{2} = −5.93 × 10^{12} J

This is almost 6 *trillion* joules given off.

? Exercise 8.8.2

The nuclear equation for the fission of uranium-238 is as follows:

$$\underset{1.0087}{^{1}_{0}\text{n}} + \underset{238.0508}{^{238}_{92}\text{U}} \rightarrow \underset{95.9342}{^{96}_{37}\text{Rb}} + \underset{134.9060}{^{135}_{55}\text{Cs}} + \underset{8\times1.0087}{8{}^{1}_{0}\text{n}}$$

The molar mass in grams of each species is given for each particle. What is the energy change of this fission reaction?

Answer

-1.35×10^{13} J

A **nuclear reactor** is an apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. Figure **8.8.1** shows a simplified diagram of a nuclear reactor. The energy from the controlled nuclear reaction converts water into high-pressure steam, which is used to run turbines that generate electricity.

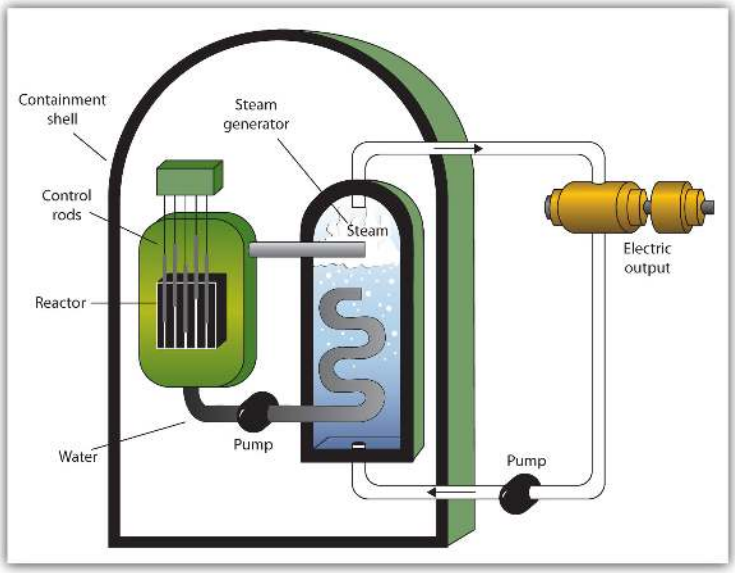


Figure **8.8.1**: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

Diagram of the nuclear power plant includes the containment shell, control rods, reactor, water, pump, steam generator, and electric output.

Although the fission of large nuclei can produce different products, on average the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a **chain reaction**.

$$1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow 256 \rightarrow 512 \rightarrow 1{,}024 \rightarrow 2{,}048 \rightarrow 4{,}096 \rightarrow 8{,}192 \rightarrow 16{,}384 \rightarrow \ldots$$

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The quick production of energy creates an explosion. This is the mechanism behind the **atomic bomb**. (The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.)

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. The enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, uranium must be enriched to 70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is hydrogen fusion, which makes helium:

$$4\,^1H \rightarrow\,^4 \text{He} + 2.58 \times 10^{12}\ J$$

Notice that the amount of energy given off per mole of reactant is only one-tenth of the amount given off by the fission of 1 mol of uranium-235. On a mass (per gram) basis, however, hydrogen fusion gives off 10 times more energy than fission does. In addition, the product of fusion is helium gas, not a wide range of isotopes (some of which are also radioactive) produced by fission.

Fusion occurs in nature: the sun and other stars use fusion as their ultimate energy source. Fusion is also the basis of very destructive weapons that have been developed by several countries around the world. However, one current goal is to develop a source of *controlled* fusion for use as an energy source. The practical problem is that to perform fusion, extremely high pressures and temperatures are necessary. Currently, the only known stable systems undergoing fusion are the interiors of stars. The conditions necessary for fusion can be created using an atomic bomb, but the resulting fusion is uncontrollable (and the basis for another type of bomb, a hydrogen bomb). Currently, researchers are looking for safe, controlled ways for producing useful energy using fusion.

Summary

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.

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