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CHEM 2CH
HONORS GENERAL
CHEMISTRY III



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UC Davis: Chem 2CH Honors General Chemistry III

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UC Davis CHE 2CH Honors General Chemistry III

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CHAPTER OVERVIEW

18: Chemical Kinetics

Topic hierarchy

- [18.1: Rates of Chemical Reactions](#)
- [18.2: Rate Laws](#)
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- [18.4: Reaction Mechanisms and Rate](#)
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18.1: Rates of Chemical Reactions

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

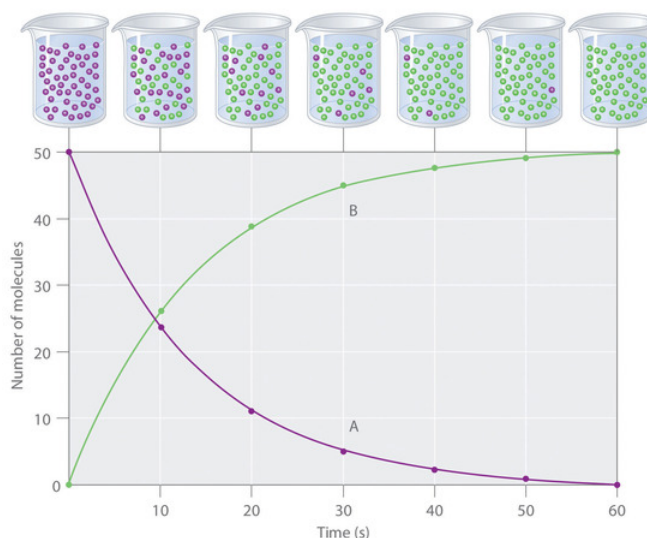


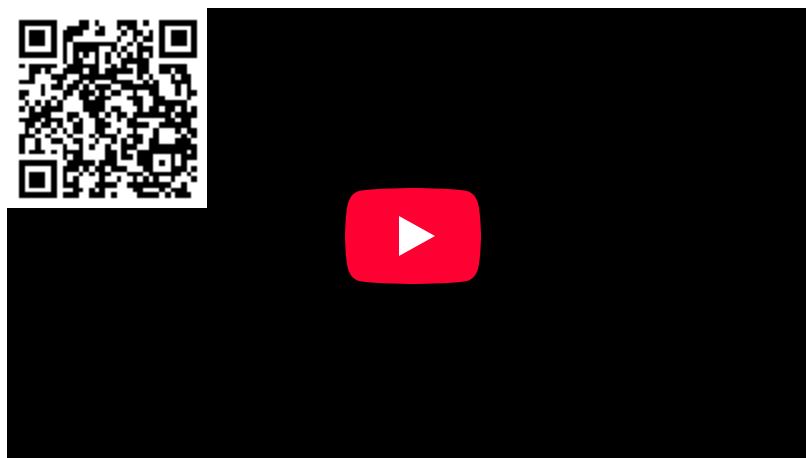
Figure 18.1.1: The Progress of a Simple Reaction ($A \rightarrow B$). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction ($A \rightarrow B$) is shown in Figure 18.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 18.1.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t} \quad (18.1.1)$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of $\Delta[A]/\Delta t$ to convert that expression to a positive number. The reaction rate calculated for the reaction $A \rightarrow B$ using Equation 18.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

Reaction rates generally decrease with time as reactant concentrations decrease.



A Video Discussing Average Reaction Rates. Video Link: [Introduction to Chemical Reaction Kinetics](#)(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 18.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 18.1.2

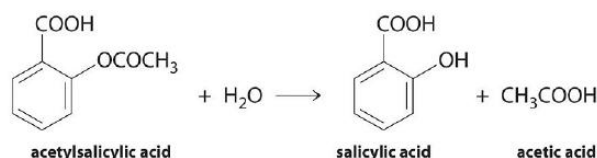


Figure 18.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 18.1.1 and are shown in the graph in Figure 18.1.3

Table 18.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 18.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

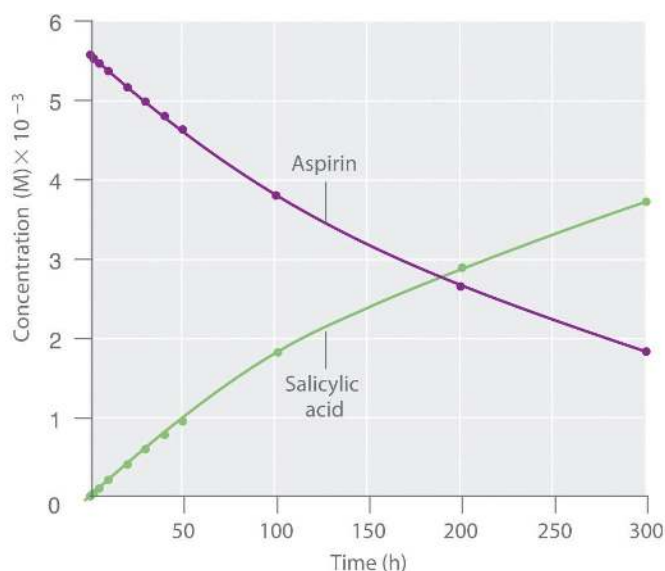


Figure 18.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between $t = 0$ h and $t = 2.0$ h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned} \text{rate}_{(t=0-2.0 \text{ h})} &= \frac{[\text{salicylic acid}]_2 - [\text{salicylic acid}]_0}{2.0 \text{ h} - 0 \text{ h}} \\ &= \frac{0.040 \times 10^{-3} \text{ M} - 0 \text{ M}}{2.0 \text{ h}} = 2.0 \times 10^{-5} \text{ M/h} \end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

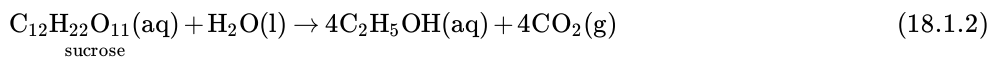
$$\begin{aligned} \text{rate}_{(t=0-2.0 \text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0 \text{ h} - 0 \text{ h}} \\ &= -\frac{(5.51 \times 10^{-3} \text{ M}) - (5.55 \times 10^{-3} \text{ M})}{2.0 \text{ h}} \\ &= 2 \times 10^{-5} \text{ M/h} \end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 18.1.1 (the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval ($t = 0-2.0$ h):

$$\begin{aligned} \text{rate}_{(t=200-300 \text{ h})} &= \frac{[\text{salicylic acid}]_{300} - [\text{salicylic acid}]_{200}}{300 \text{ h} - 200 \text{ h}} \\ &= \frac{(3.73 \times 10^{-3} \text{ M}) - (2.91 \times 10^{-3} \text{ M})}{100 \text{ h}} \\ &= 8.2 \times 10^{-6} \text{ M/h} \end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:



The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[\text{C}_2\text{H}_5\text{OH}]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \quad (18.1.3)$$

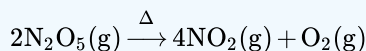
The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of $\Delta[\text{sucrose}]$ is negative. Consequently, a minus sign is inserted in front of $\Delta[\text{sucrose}]$ in Equation 18.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 18.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4} \left(\frac{\Delta[\text{C}_2\text{H}_5\text{OH}]}{\Delta t} \right) \quad (18.1.4)$$

✓ Example 18.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:



Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

- Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
- For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

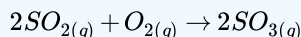
A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[\text{N}_2\text{O}_5]$ and $[\text{NO}_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2 , the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

? Exercise 18.1.1: Contact Process I

The **contact process** is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3 .



Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

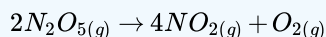
The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, $t = 0$. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to $t = 0$.



✓ Example 18.1.2: Decomposition Reaction II

Using the reaction shown in Example 18.1.1, calculate the reaction rate from the following data taken at 56°C:



calculate the reaction rate from the following data taken at 56°C:

Time (s)	[N ₂ O ₅] (M)	[NO ₂] (M)	[O ₂] (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

- Using the equations in Example 18.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
- Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between $t_1 = 240$ s and $t_2 = 600$ s. From Example 18.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N₂O₅ and inserting the corresponding time interval into the rate expression for N₂O₅,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600 \text{ s} - 240 \text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197 \text{ M} - 0.0388 \text{ M}}{2(360 \text{ s})} = 2.65 \times 10^{-5} \text{ M/s}$$

Similarly, NO₂ can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600 \text{ s} - 240 \text{ s})} = \frac{0.0699 \text{ M} - 0.0314 \text{ M}}{4(360 \text{ s})} = 2.67 \times 10^{-5} \text{ M/s}$$

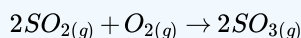
Allowing for experimental error, this is the same rate obtained using the data for N₂O₅. The data for O₂ can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600 \text{ s} - 240 \text{ s}} = \frac{0.0175 \text{ M} - 0.00792 \text{ M}}{360 \text{ s}} = 2.66 \times 10^{-5} \text{ M/s}$$

Again, this is the same value obtained from the N₂O₅ and NO₂ data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 18.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of SO₂(g) with O₂(g) to give SO₃(g).



calculate the reaction rate of SO₂(g) with O₂(g) to give SO₃(g).

Time (s)	[SO ₂] (M)	[O ₂] (M)	[SO ₃] (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

$$9.0 \times 10^{-6} \text{ M/s}$$

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for $A \rightarrow B$:

$$\text{rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

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18.2: Rate Laws

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \quad (18.2.1)$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k , a positive value.

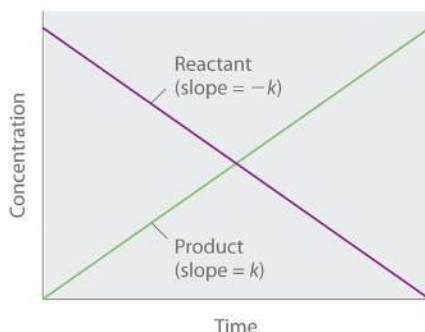


Figure 18.2.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k . The product is in green and has a slope of positive k .

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \quad (18.2.2)$$

where $[A]_0$ is the initial concentration of reactant A . Equation 18.2.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the

decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2 , which occurs at temperatures ranging from 200°C to 400°C :



Without a platinum surface, the reaction requires temperatures greater than 700°C , but between 200°C and 400°C , the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O , where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2} \left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t} \right) = \frac{1}{2} \left(\frac{\Delta[\text{N}_2]}{\Delta t} \right) = \frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{N}_2\text{O}]^0 = k \quad (18.2.4)$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 18.2.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

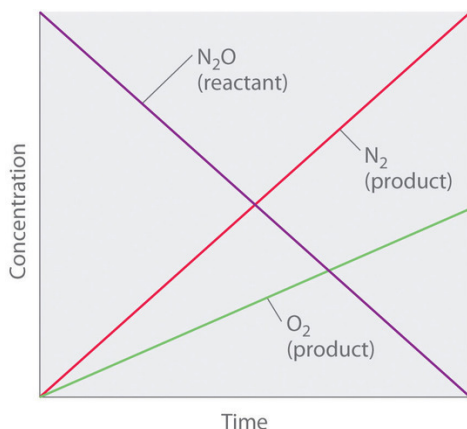


Figure 18.2.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N_2O is the reactant is graphed in purple. O_2 is one of the products and is graphed in green. The second product is N_2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

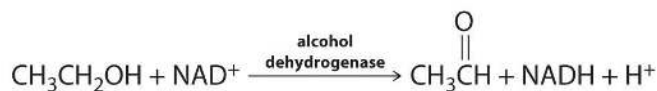


Figure 18.2.2

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure 18.2.3a). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 18.2.3).

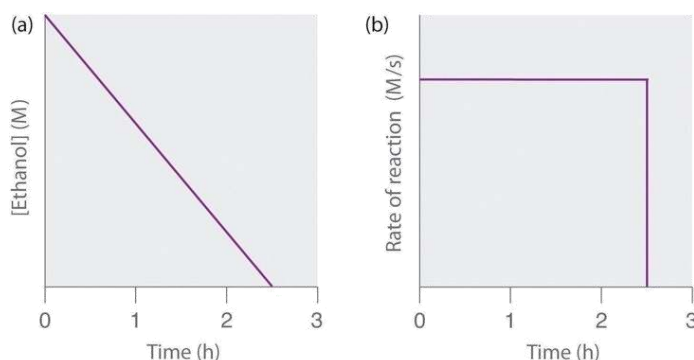


Figure 18.2.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form $A \rightarrow \text{products}$. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad (18.2.5)$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \quad (18.2.6)$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 18.2.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 18.2.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t :

$$\ln[A] = \ln[A]_0 - kt \quad (18.2.7)$$

Because Equation 18.2.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 18.2.5) or the integrated rate law (Equation 18.2.7) can be used to determine whether a particular reaction is first order.

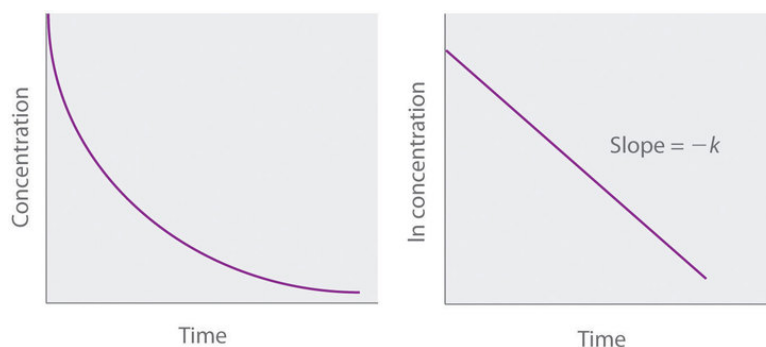


Figure 18.2.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

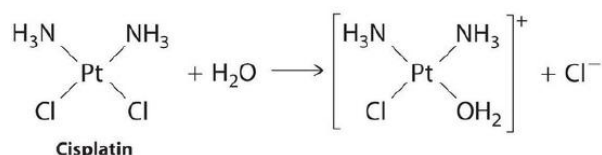


Figure 18.2.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 18.2.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 18.2.4 have been studied extensively to find ways of maximizing the concentration of the active species.

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 18.2.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 18.2.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	[Cisplatin] ₀ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 18.2.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 2.0$] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 5.0$] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is $\text{rate} = k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 18.2.1. For example, substituting the values for Experiment 3 into Equation 18.2.5,

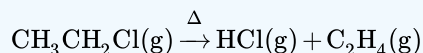
$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

✓ Example 18.2.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:



Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[\text{CH}_3\text{CH}_2\text{Cl}]_0 \text{ (M)}$	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

- Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
- Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[\text{CH}_3\text{CH}_2\text{Cl}]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[\text{CH}_3\text{CH}_2\text{Cl}]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is $\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}]$.

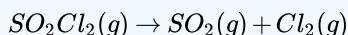
C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})$$

$$1.6 \times 10^{-6} \text{ s}^{-1} = k$$

? Exercise 18.2.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:



Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	[SO ₂ Cl ₂] ₀ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure 18.2.6a shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

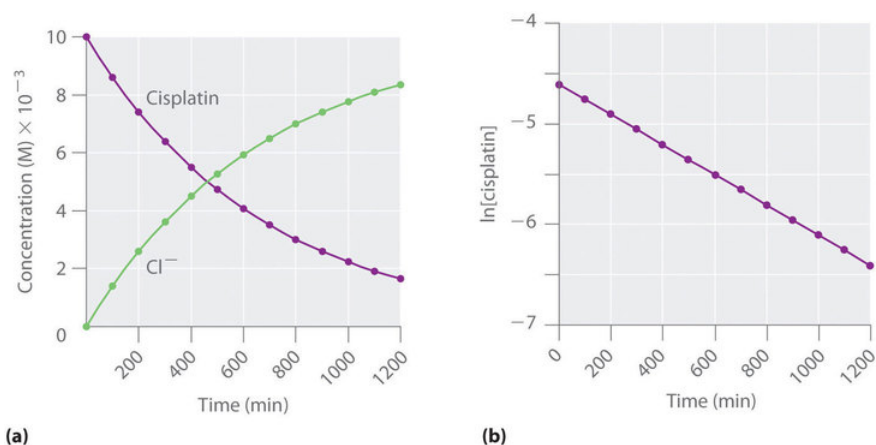


Figure 18.2.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 18.2.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 18.2.6 for $t = 100 \text{ min}$ ($[\text{cisplatin}] = 0.0086 \text{ M}$) and $t = 1000 \text{ min}$ ($[\text{cisplatin}] = 0.0022 \text{ M}$),

$$\begin{aligned} \text{slope} &= \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000 \text{ min} - 100 \text{ min}} \\ -k &= \frac{\ln 0.0022 - \ln 0.0086}{1000 \text{ min} - 100 \text{ min}} = \frac{-6.12 - (-4.76)}{900 \text{ min}} = -1.51 \times 10^{-3} \text{ min}^{-1} \\ k &= 1.5 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 18.2.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



Video Example Using the First-Order Integrated Rate Law Equation:

[Example Using the First-Order Integrated Rate Law Equation](#)(opens in new window) [youtu.be]

✓ Example 18.2.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6} \text{ s}^{-1}$) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

- Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ($[A]$) at the given time t .
- Given a concentration $[A]$, solve the integrated rate law for time t .

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 18.2.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6} \text{ s}^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time t . Substituting the known values into the integrated rate law,

$$\begin{aligned} [\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= [\text{CH}_3\text{CH}_2\text{Cl}]_0 e^{-kt} \\ &= 0.0200 \text{ M} (e^{-(1.6 \times 10^{-6} \text{ s}^{-1})[(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})]}) \\ &= 0.0189 \text{ M} \end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 18.2.7):

$$\begin{aligned} \ln[\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6} \text{ s}^{-1})[(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})] \\ &= -3.912 - 0.0576 = -3.970 \\ [\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= e^{-3.970} \text{ M} \\ &= 0.0189 \text{ M} \end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t . Equation 18.2.7 gives the following:

$$\ln[\text{CH}_3\text{CH}_2\text{Cl}]_t = \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - kt$$

$$kt = \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - \ln[\text{CH}_3\text{CH}_2\text{Cl}]_t = \ln \frac{[\text{CH}_3\text{CH}_2\text{Cl}]_0}{[\text{CH}_3\text{CH}_2\text{Cl}]_t}$$

$$t = \frac{1}{k} \left(\ln \frac{[\text{CH}_3\text{CH}_2\text{Cl}]_0}{[\text{CH}_3\text{CH}_2\text{Cl}]_t} \right) = \frac{1}{1.6 \times 10^{-6} \text{ s}^{-1}} \left(\ln \frac{0.0200 \text{ M}}{0.0050 \text{ M}} \right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6} \text{ s}^{-1}} = 8.7 \times 10^5 \text{ s} = 240 \text{ h} = 2.4 \times 10^2 \text{ h}$$

? Exercise 18.2.2

In the exercise in Example 18.2.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C .

- Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C .
- How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

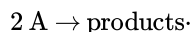
0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form



A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form $\text{A} + \text{B} \rightarrow \text{products}$. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which $2\text{A} \rightarrow \text{products}$ is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{2\Delta t} = k[\text{A}]^2 \quad (18.2.8)$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($\text{M}^{-1}\cdot\text{s}^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as $\text{L}(\text{mol}\cdot\text{s})$.

For the reaction $2\text{A} \rightarrow \text{products}$, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt \quad (18.2.9)$$

Because Equation 18.2.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[\text{A}]$ and $b = 1/[\text{A}]_0$, a plot of $1/[\text{A}]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[\text{A}]_0$.

Second-order reactions generally have the form $2\text{A} \rightarrow \text{products}$ or $\text{A} + \text{B} \rightarrow \text{products}$.



Video Discussing the Second-Order Integrated Rate Law Equation: [Second-Order Integrated Rate Law Equation](#)(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2 . Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

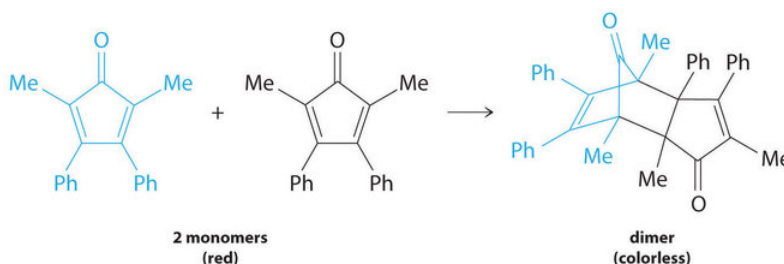


Figure 18.2.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is $2A \rightarrow \text{product}$. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 18.2.8) or the integrated rate law (Equation 18.2.9).

Table 18.2.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 18.2.2. From the data, we see that the reaction rate is not independent of the monomer

concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5} \text{ M/min}}{1.8 \times 10^{-5} \text{ M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3} \text{ M}}{2.0 \times 10^{-3} \text{ M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 18.2.8 and the data from any row in Table 18.2.2 we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \quad (18.2.10)$$

$$8.0 \times 10^{-5} \text{ M/min} = k(4.4 \times 10^{-3} \text{ M})^2 \quad (18.2.11)$$

$$4.1 \text{ M}^{-1} \cdot \text{min}^{-1} = k \quad (18.2.12)$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 18.2.8a. The measurements show that the concentration of the monomer (initially $5.4 \times 10^{-3} \text{ M}$) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of $1/[\text{monomer}]$ versus t should be a straight line, as shown in Figure 18.2.8b. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1 \text{ M}^{-1} \cdot \text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

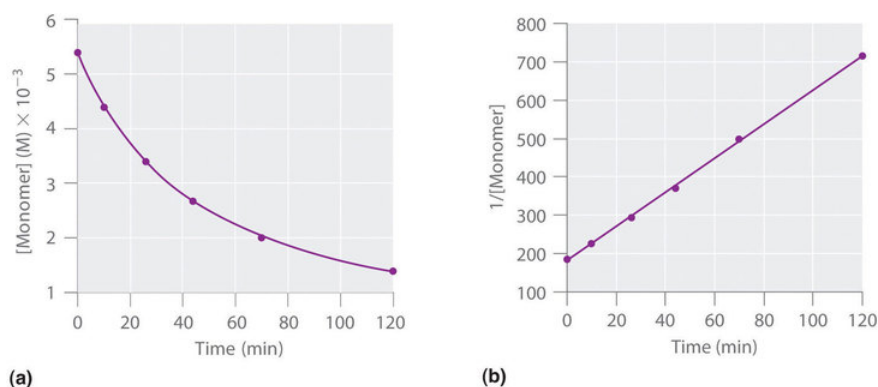
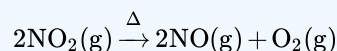


Figure 18.2.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) $1/[\text{monomer}]$ versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

✓ Example 18.2.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.



Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO_2

Experiment	$[\text{NO}_2]_0 (\text{M})$	Initial Rate (M/s)
1	0.015	1.22×10^{-4}

Experiment	[NO ₂] ₀ (M)	Initial Rate (M/s)
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

- From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
- Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

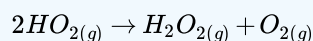
A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO₂ concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to [NO₂]². Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to [NO₂]². This behavior is characteristic of a second-order reaction.

B We have rate = $k[\text{NO}_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned}\text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5} \text{ M/s} &= k(0.010 \text{ M})^2 \\ 0.54 \text{ M}^{-1} \cdot \text{s}^{-1} &= k\end{aligned}$$

? Exercise 18.2.3

When the highly reactive species HO₂ forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:



The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	[HO ₂] ₀ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO₂; $k = 1.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of $1/(\text{reactant concentration})$ versus time is linear, then the reaction is second order.

✓ Example 18.2.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C , what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

- Given k , t , and $[\text{A}]_0$, use the integrated rate law for a second-order reaction to calculate $[\text{A}]$.
- Setting $[\text{A}]$ equal to 1/10 of $[\text{A}]_0$, use the same equation to solve for t .

Solution

A We know k and $[\text{NO}_2]_0$, and we are asked to determine $[\text{NO}_2]$ at $t = 1 \text{ h}$ (3600 s). Substituting the appropriate values into Equation 18.2.9,

$$\begin{aligned}\frac{1}{[\text{NO}_2]_{3600}} &= \frac{1}{[\text{NO}_2]_0} + kt \\ &= \frac{1}{0.056 \text{ M}} + [(0.54 \text{ M}^{-1} \cdot \text{s}^{-1})(3600 \text{ s})] \\ &= 2.0 \times 10^3 \text{ M}^{-1}\end{aligned}$$

Thus $[\text{NO}_2]_{3600} = 5.1 \times 10^{-4} \text{ M}$.

B In this case, we know k and $[\text{NO}_2]_0$, and we are asked to calculate at what time $[\text{NO}_2] = 0.1[\text{NO}_2]_0 = 0.1(0.056 \text{ M}) = 0.0056 \text{ M}$. To do this, we solve Equation 18.2.9 for t , using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[\text{NO}_2]) - (1/[\text{NO}_2]_0)}{k} \\ &= \frac{(1/0.0056 \text{ M}) - (1/0.056 \text{ M})}{0.54 \text{ M}^{-1} \cdot \text{s}^{-1}} \\ &= 3.0 \times 10^2 \text{ s} = 5.0 \text{ min}\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

? Exercise 18.2.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2 , calculate the concentration of HO_2 that remains after 1.0 h at 25°C . How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated in the exercise in Example 18.2.3

Answer

$$2.0 \times 10^{-13} \text{ M}; 6.4 \times 10^{-6} \text{ s}$$

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow \text{products}$, in which the reaction is first order in A and first order in B . The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = k[A][B]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k \\ [A] &= [A]_0 - kt\end{aligned}$$

- **first-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k[A] \\ [A] &= [A]_0 e^{-kt} \\ \ln[A] &= \ln[A]_0 - kt\end{aligned}$$

- **second-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k[A]^2 \\ \frac{1}{[A]} &= \frac{1}{[A]_0} + kt\end{aligned}$$

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- [14.4: The Change of Concentration with Time \(Integrated Rate Laws\)](#) is licensed [CC BY-NC-SA 3.0](#).

18.3: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

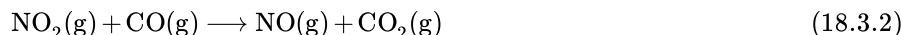


For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

The overall sequence of elementary reactions is the mechanism of the reaction.

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.



From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$\text{rate} = k[\text{NO}_2]^2 \quad (18.3.3)$$

The fact that the reaction is second order in $[\text{NO}_2]$ and independent of $[\text{CO}]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$\text{rate} = k[\text{NO}_2][\text{CO}].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

two-step mechanism		
step 1	$\text{NO}_2 + \text{NO}_2 \xrightarrow{\text{slow}} \text{NO}_3 + \text{NO}$	elementary reaction
step 2	$\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$	elementary reaction
sum	$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

*The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

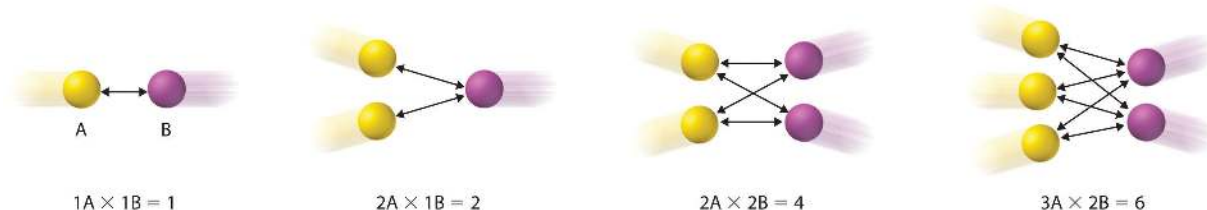


Figure 18.3.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 18.3.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction ($A \rightarrow \text{products}$) is

$$\text{rate} = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 18.3.1. For a bimolecular elementary reaction of the form $A + B \rightarrow \text{products}$, the general rate law is

$$\text{rate} = k[A][B].$$

Table 18.3.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
$A \rightarrow \text{products}$	unimolecular	$\text{rate} = k[A]$	first
$2A \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A]^2$	second
$A + B \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A][B]$	second
$2A + B \rightarrow \text{products}$	termolecular	$\text{rate} = k[A]^2[B]$	third
$A + B + C \rightarrow \text{products}$	termolecular	$\text{rate} = k[A][B][C]$	third

*For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction. This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the

experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$\text{NO}_2 + \text{NO}_2 \xrightarrow{k_1} \text{NO}_3 + \text{NO}$	rate = $k_1[\text{NO}_2]^2$ (predicted)
step 2	$\text{NO}_3 + \text{CO} \xrightarrow{k_2} \text{NO}_2 + \text{CO}_2$	rate = $k_2[\text{NO}_3][\text{CO}]$ (predicted)
sum	$\text{NO}_2 + \text{CO} \xrightarrow{k} \text{NO} + \text{CO}_2$	rate = $k[\text{NO}_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1 . That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

✓ Example 18.3.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$\text{NO}_2 + \text{NO}_2 \xrightarrow{k_1} \text{N}_2\text{O}_4$
step 2	$\text{N}_2\text{O}_4 + \text{CO} \xrightarrow{k_2} \text{NO} + \text{NO}_2 + \text{CO}_2$
sum	$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[\text{NO}_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

- Determine the rate law for each elementary reaction in the reaction.
- Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

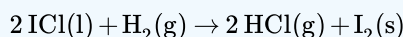
Solution

A The rate law for step 1 is $\text{rate} = k_1[\text{NO}_2]^2$; for step 2, it is $\text{rate} = k_2[\text{N}_2\text{O}_4][\text{CO}]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: $\text{rate} = k_1[\text{NO}_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4 , directly.

? Exercise 18.3.1

Iodine monochloride (ICl) reacts with H_2 as follows:



The experimentally determined rate law is $\text{rate} = k[\text{ICl}][\text{H}_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$\text{ICl} + \text{H}_2 \xrightarrow{k_1} \text{HCl} + \text{HI}$	$\text{rate} = k_1[\text{ICl}][\text{H}_2]$ (slow)
step 2	$\text{HI} + \text{ICl} \xrightarrow{k_2} \text{HCl} + \text{I}_2$	$\text{rate} = k_2[\text{HI}][\text{ICl}]$ (fast)
sum	$2\text{ICl} + \text{H}_2 \rightarrow 2\text{HCl} + \text{I}_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

✓ Example 18.3.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$\text{NO} + \text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2$	(fast)
step 2	$\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$	(slow)
step 3	$\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

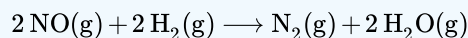
$$\text{rate} = k[\text{NO}]^2[\text{H}_2] \quad (\text{observed})$$

Answer

- Step 1: $\text{rate} = k_1[\text{NO}]^2$
- Step 2: $\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$

- Step 3: $rate = k_3[N_2O][H_2]$

The overall reaction is then



- Rate Determining Step : #2
- Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting $k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.



Reaction Mechanism (Slow step followed by fast step): [Reaction Mechanism \(Slow step Followed by Fast Step\)](#)(opens in new window) [youtu.be] ([opens in new window](#))

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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18.4: Reaction Mechanisms and Rate

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18.5: Effect of Temperature on Reaction Rates

Learning Objectives

- To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is [straightforward](#), it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \quad (18.5.1)$$

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B , respectively
- k_B is the Boltzmann constant $k_B = 1.380 \times 10^{-23}$ Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 18.5.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via [Kinetic Molecular Theory](#)), and with increasing temperature (although weakly because of the square root function).

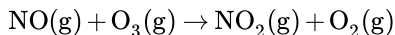


A Video Discussing Collision Theory of Kinetics: [Collusion Theory of Kinetics \(opens in new window\)](#) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy** (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:



Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

Experimental rate law for this reaction is

$$\text{rate} = k[\text{NO}][\text{O}_3]$$

and is used to identify how the reaction rate (not the rate constant) varies with concentration. The rate constant, however, does vary with temperature. Figure 18.5.1 shows a plot of the rate constant of the reaction of NO with O₃ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g., the [Clausius-Claperyon equation](#)). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

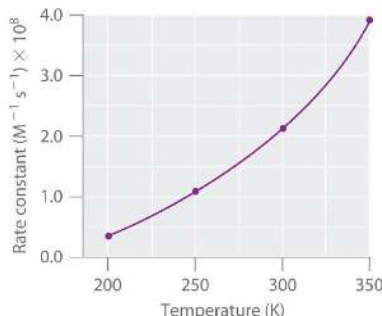


Figure 18.5.1: Rate Constant versus Temperature for the Reaction of NO with O₃ The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the **activation energy**, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 18.5.2 shows a plot for the NO–O₃ system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is –200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

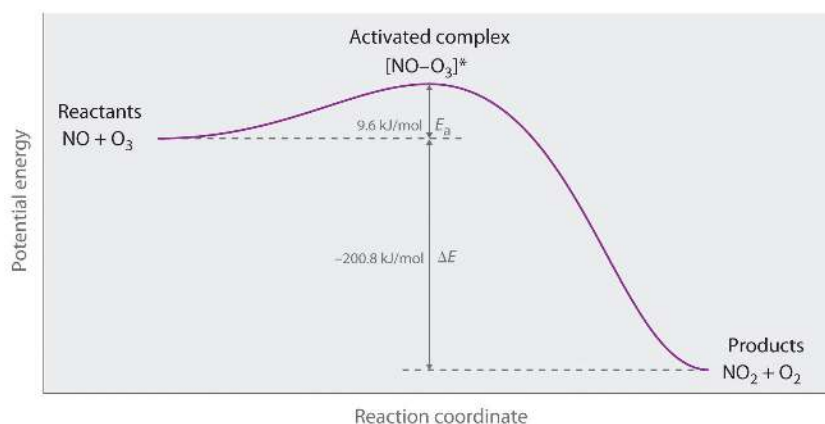


Figure 18.5.2: Energy of the Activated Complex for the NO–O₃ System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure 18.5.3a illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure 18.5.3b illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and ($\Delta E > 0$). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.

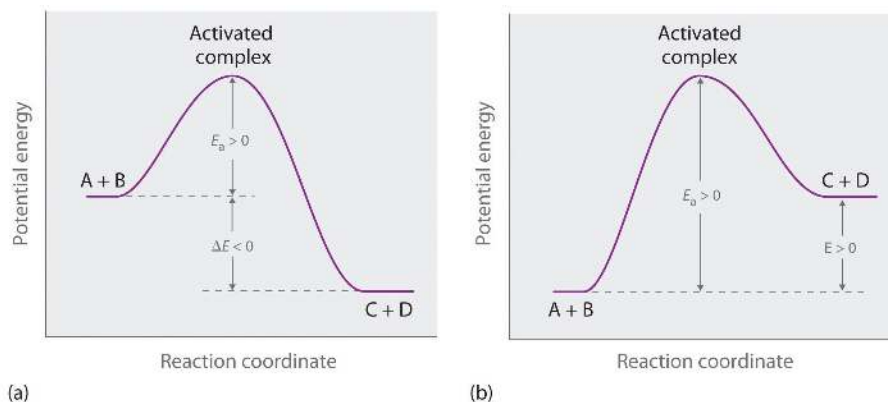


Figure 18.5.3: Differentiating between E_a and ΔE . The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE . (CC BY-SA-NC; anonymous)

For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with

the smallest E_a will occur more rapidly.

Figure 18.5.4 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a ; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a . Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

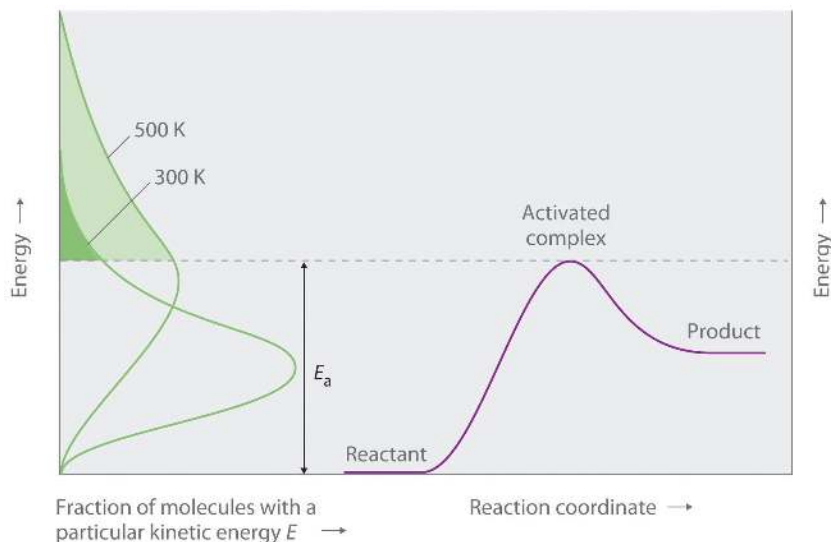


Figure 18.5.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.



Video Discussing Transition State Theory: [Transition State Theory](https://chem.libretexts.org/@go/page/44484)(opens in new window) [youtu.be]

Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a , most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2 , a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 18.5.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a , most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).

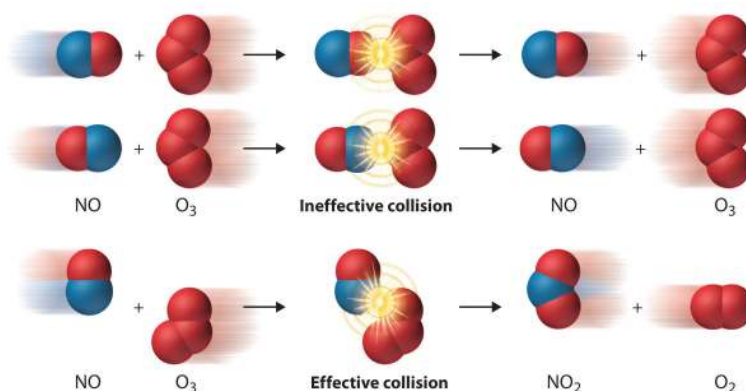


Figure 18.5.4: The Effect of Molecular Orientation on the Reaction of NO and O₃. Most collisions of NO and O₃ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O₃ are likely to produce NO₂ and O₂, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO₂ a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \quad (18.5.2)$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A , called the **frequency factor**:

$$k = Ae^{-E_a/RT} \quad (18.5.3)$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 18.5.1). Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

Equation 18.5.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 18.5.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT} \right) \quad (18.5.4)$$

$$= \ln A + \left[\left(-\frac{E_a}{R} \right) \left(\frac{1}{T} \right) \right] \quad (18.5.5)$$

Equation 18.5.5 is the equation of a straight line,

$$y = mx + b$$

where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a .

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 18.5.1.



A Video Discussing The Arrhenius Equation: [The Arrhenius Equation](#)(opens in new window) [youtu.be]

✓ Example 18.5.1: Chirping Tree Crickets

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of $\ln[\text{chirping rate}]$ versus $1/T$ to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Chirping Tree Crickets Frequency Table

Frequency (f ; chirps/min)	$\ln f$	T (K)	$1/T$ (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

- From the plot of $\ln f$ versus $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
- Express Equation 18.5.5 in terms of k_1 and T_1 and then in terms of k_2 and T_2 .
- Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1 .

D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1 . Using the value listed in the table for k_1 , solve for k_2 .

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 18.5.6).

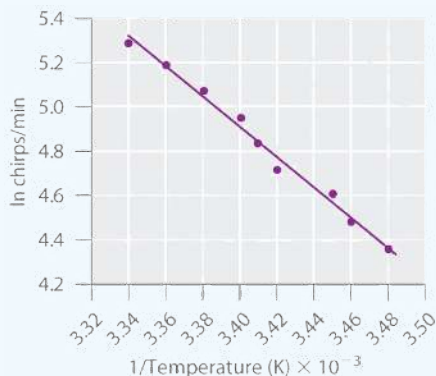


Figure 18.5.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus $1/T$, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 18.5.6 to estimate the slope:

$$\begin{aligned} \text{slope} &= \frac{\Delta \ln f}{\Delta(1/T)} \\ &= \frac{5.30 - 4.37}{3.34 \times 10^{-3} \text{ K}^{-1} - 3.48 \times 10^{-3} \text{ K}^{-1}} \\ &= \frac{0.93}{-0.14 \times 10^{-3} \text{ K}^{-1}} \\ &= -6.6 \times 10^3 \text{ K} \end{aligned}$$

A computer best-fit line through all the points has a slope of $-6.67 \times 10^3 \text{ K}$, so our estimate is very close. We now use it to solve for the activation energy:

$$\begin{aligned} E_a &= -(\text{slope})(R) \\ &= -(-6.6 \times 10^3 \text{ K}) \left(\frac{8.314 \text{ J}}{\text{K} \cdot \text{mol}} \right) \left(\frac{1 \text{ KJ}}{1000 \text{ J}} \right) \\ &= \frac{55 \text{ kJ}}{\text{mol}} \end{aligned}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 18.5.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

C These two equations contain four known quantities (E_a , T_1 , T_2 , and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\begin{aligned}\ln k_2 - \ln k_1 &= \left(\ln A - \frac{E_a}{RT_2} \right) - \left(\ln A - \frac{E_a}{RT_1} \right) \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}\end{aligned}$$

Then

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

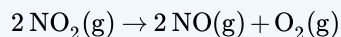
D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for $T_1 = 296$ K, where $f = 158$, and using the E_a calculated previously,

$$\begin{aligned}\ln \frac{k_{T_2}}{k_{T_1}} &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{55 \text{ kJ/mol}}{8.314 \text{ J/(K} \cdot \text{mol)}} \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) \left(\frac{1}{296 \text{ K}} - \frac{1}{308 \text{ K}} \right) \\ &= 0.87\end{aligned}$$

Thus $k_{308}/k_{296} = 2.4$ and $k_{308} = (2.4)(158) = 380$, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

? Exercise 18.5.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2 :



Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

Data for the reaction rate as a function of temperature

T (K)	k ($\text{M}^{-1}\cdot\text{s}^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

$$E_a = 114 \text{ kJ/mol}; k_{700} = 18,600 \text{ M}^{-1}\cdot\text{s}^{-1} = 1.86 \times 10^4 \text{ M}^{-1}\cdot\text{s}^{-1}.$$

? Exercise 18.5.1B

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C ?

Answer

about 51 kJ/mol



A Video Discussing Graphing Using the Arrhenius Equation: [Graphing Using the Arrhenius Equation \(opens in new window\)](#)
[youtu.be] ([opens in new window](#))

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k = Ae^{-E_a/RT}$. A minimum energy (activation energy, E_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a , the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

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18.6: A Deeper Look: Reaction Dynamics

under construction

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18.7: Kinetics of Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a , but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 18.7.1). Nevertheless, because of its lower E_a , the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

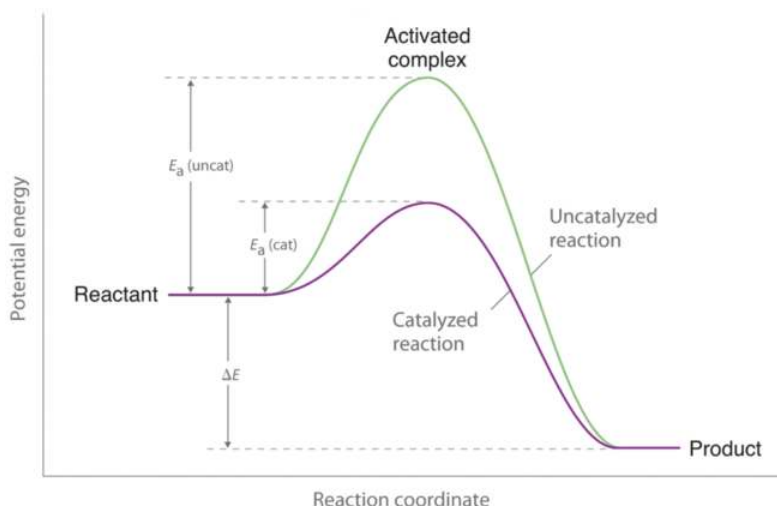


Figure 18.7.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

A catalyst affects E_a , not ΔE .

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 18.7.2 the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

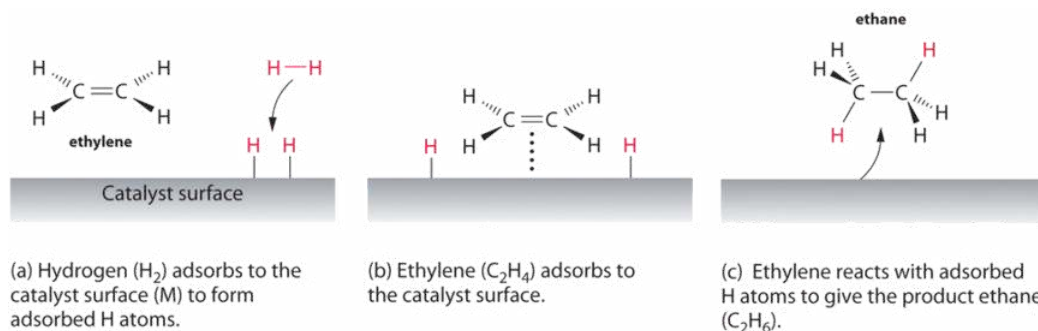


Figure 18.7.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2 . When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 18.7.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 18.7.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 18.7.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$	H_2SO_4
Haber process	Fe, K_2O , Al_2O_3	$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	NH_3
Ostwald process	Pt and Rh	$4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3 , or Cu	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	H_2 for NH_3 , CH_3OH , and other fuels
steam reforming	Ni	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	CH_3OH
Sohio process	bismuth phosphomolybdate	$\text{CH}_2=\text{CHCH}_3 + \text{NH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{CH}_2=\text{CHCN} + 3\text{H}_2\text{O}$	acrylonitrile
catalytic hydrogenation	Ni, Pd, or Pt	$\text{RCH}=\text{CHR}' + \text{H}_2 \rightarrow \text{RCH}_2\text{—CH}_2\text{R}'$	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 18.7.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 18.7.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[\text{Rh}(\text{CO})_2\text{I}_2]^-$	$\text{CO} + \text{CH}_3\text{OH}$	$\text{CH}_3\text{CO}_2\text{H}$
hydroperoxide process	Mo(VI) complexes	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{R}-\text{O}-\text{O}-\text{H}$	$\begin{array}{c} \text{CH}_3\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{O} \end{array} + \text{ROH}$ propylene oxide
hydroformylation	Rh/ PR_3 complexes	$\text{RCH}=\text{CH}_2 + \text{CO} + \text{H}_2$	$\text{RCH}_2\text{CH}_2\text{CHO}$
adiponitrile process	Ni/ PR_3 complexes	$2\text{HCN} + \text{CH}_2=\text{CHCH}=\text{CH}_2$	$\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$ used to synthesize nylon
olefin polymerization	$(\text{RC}_5\text{H}_5)_2\text{ZrCl}_2$	$\text{CH}_2=\text{CH}_2$	$-(\text{CH}_2\text{CH}_2-)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombardier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 18.7.3).



Figure 18.7.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2 .

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large

increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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CHAPTER OVERVIEW

19: Nuclear Chemistry

Nuclear chemistry is the subfield of chemistry dealing with radioactivity, nuclear processes, such as nuclear transmutation, and nuclear properties. It includes the study of the chemical effects resulting from the absorption of radiation within living animals, plants, and other materials.

Topic hierarchy

[19.1: Mass-Energy Relationships in Nuclei](#)

[19.2: Nuclear Decay Processes](#)

[19.3: Kinetics of Radioactive Decay](#)

[19.4: Radiation in Biology and Medicine](#)

[19.5: Nuclear Fission](#)

[19.6: Nuclear Fusion and Nucleosynthesis](#)

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19.1: Mass-Energy Relationships in Nuclei

Learning Objectives

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

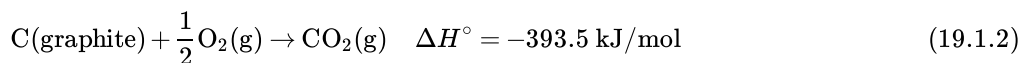
The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \quad (19.1.1)$$

where

- c is the speed of light ($2.998 \times 10^8 \text{ m/s}$), and
- E and m are expressed in units of joules and kilograms, respectively.

Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 19.1.1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:



Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH . When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE . For most chemical reactions, however, $\Delta E \approx \Delta H$. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \quad (19.1.3)$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \quad (19.1.4)$$

Because $1 \text{ J} = 1 (\text{kg} \cdot \text{m}^2)/\text{s}^2$, the change in mass is as follows:

$$\Delta m = \frac{-393.5 \text{ kJ/mol}}{(2.998 \times 10^8 \text{ m/s})^2} = \frac{-3.935 \times 10^5 (\text{kg} \cdot \text{m}^2)/(\text{s}^2 \cdot \text{mol})}{(2.998 \times 10^8 \text{ m/s})^2} = -4.38 \times 10^{-12} \text{ kg/mol} \quad (19.1.5)$$

This is a mass change of about $3.6 \times 10^{-10} \text{ g/g}$ carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:



We can use the experimentally measured masses of subatomic particles and common isotopes given in Table 20.1 to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \quad (19.1.7)$$

$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \quad (19.1.8)$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is $-0.000168 \text{ g} = -1.68 \times 10^{-4} \text{ g} = -1.68 \times 10^{-7} \text{ kg}$. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \quad (19.1.9)$$

$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^7 \text{ kJ} \quad (19.1.10)$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4} \text{ amu}) \left(\frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV}$$

✓ Example 19.1.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 19.1.4 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution

A Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } ^4_2\text{He}) - \text{mass } ^{238}\text{U} \quad (19.1.11)$$

$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \quad (19.1.12)$$

B Thus the change in mass for 1 mol of ^{238}U is -0.004584 g or $-4.584 \times 10^{-6} \text{ kg}$. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 = -4.120 \times 10^{11} \text{ J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3} \text{ amu} \times \frac{931 \text{ MeV}}{\text{amu}} \times \frac{1 \times 10^6 \text{ eV}}{1 \text{ MeV}} = -4.27 \times 10^6 \text{ eV/atom}$$

? Exercise 19.1.1

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^3H) to ^3He and a β particle.

Answer

$$\Delta m = -2.0 \times 10^{-5} \text{ amu}; \Delta E = -1.9 \times 10^6 \text{ kJ/mol} = -19 \text{ keV/atom}$$

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^1H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^2H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2\text{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \quad (19.1.13)$$

$$= 1.008665 \text{ amu} + 1.007276 \text{ amu} + 0.000549 \text{ amu} = 2.016490 \text{ amu} \quad (19.1.14)$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 19.1.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

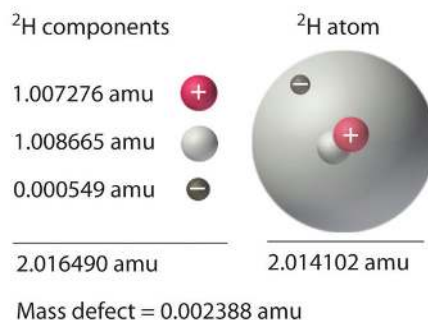


Figure 19.1.1: Nuclear Binding Energy in Deuterium. The mass of a ^2H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 19.1.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 19.1.2, the binding energy per nucleon increases rapidly with increasing atomic number until about $Z = 26$, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^4He , ^{12}C , and ^{16}O). As mentioned earlier, these are particularly stable combinations.

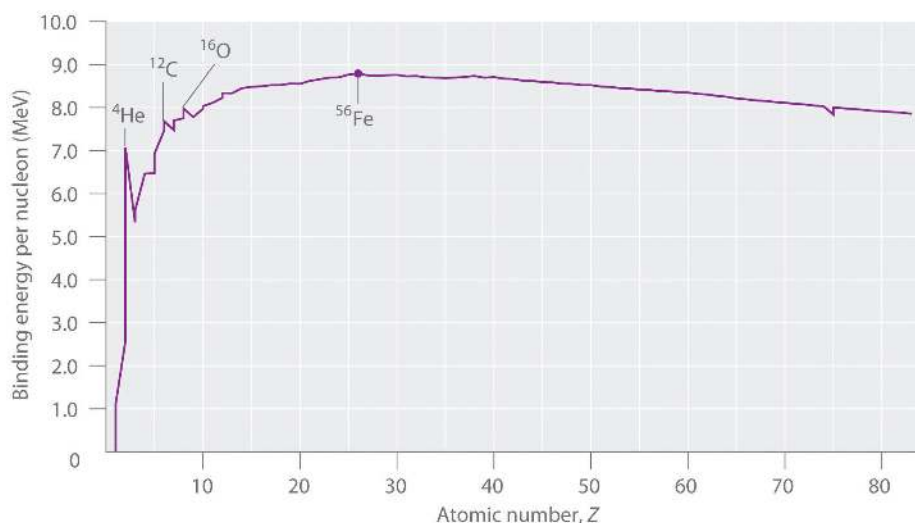


Figure 19.1.2: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about $Z = 26$, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Because the maximum binding energy per nucleon is reached at ^{56}Fe , all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe . Consequently, heavier nuclei (toward the right in Figure 19.1.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 19.1.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.

✓ Example 19.1.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe . The experimental mass of the nuclide is given in Table A4.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^1H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^1H atoms, we can calculate the sum of the masses more quickly as follows:

$$\begin{aligned}\text{calculated mass} &= 26(\text{mass } ^1_1\text{H}) + 30(\text{mass } ^1_0\text{n}) \\ &= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400\text{ amu} \\ \text{experimental mass} &= 55.934938\end{aligned}$$

B We subtract to find the mass defect:

$$\begin{aligned}\text{mass defect} &= \text{calculated mass} - \text{experimental mass} \\ &= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu}\end{aligned}$$

C The nuclear binding energy is thus $0.528462 \text{ amu} \times 931 \text{ MeV/amu} = 492 \text{ MeV}$. The binding energy per nucleon is $492 \text{ MeV}/56 \text{ nucleons} = 8.79 \text{ MeV/nucleon}$.

? Exercise 19.1.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U .

Answer

1800 MeV/ ^{238}U ; 7.57 MeV/nucleon

Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^1H , the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

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19.2: Nuclear Decay Processes

Learning Objectives

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^1H), which accounts for about 90% of all atoms. In fact, ^1H is the raw material from which all other elements are formed. In this section, we explain why ^1H and ^4He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 19.2.1. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure 19.2.1 illustrate two important points. First, except for hydrogen, the most abundant elements have even atomic numbers. Not only is this consistent with the known trends in nuclear stability, but it also suggests that heavier elements are formed by combining helium nuclei ($Z = 2$). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 19.2.1 for some common elements.

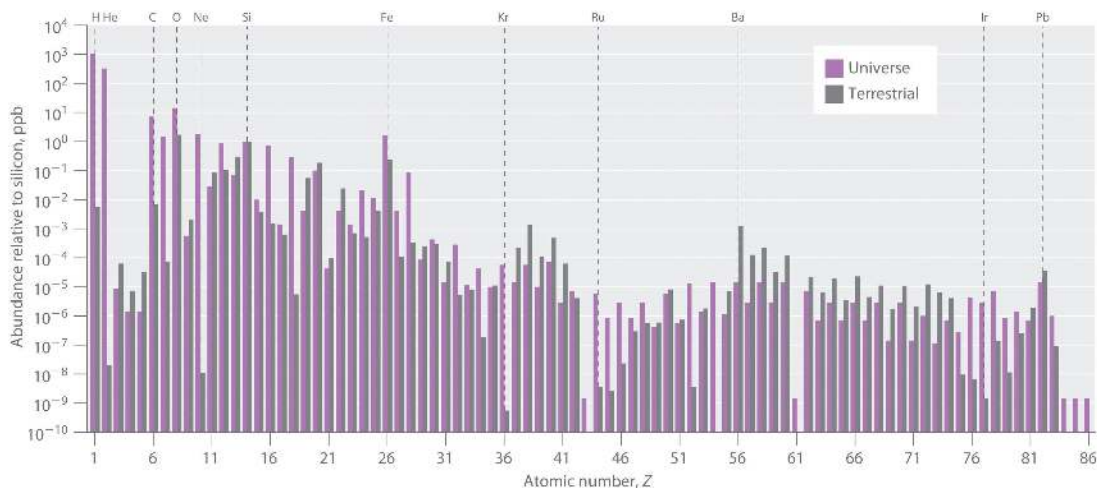


Figure 19.2.1: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth. (CC BY-NC-SA 3.0; anonymous)

Bar graph of abundance relative to silicon in pbb against atomic number. The purple bars are universe elements while the gray bars are terrestrial elements.

Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3 , CH_4 , and H_2O . Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K . In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much less abundant on Earth than in the universe; some examples are Ru and Ir. This section explains some of the reasons for the great differences in abundances of the metallic elements.

Table 19.2.1: Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 19.2.2). Initially, all stars are formed by the aggregation of interstellar “dust,” which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3 , and the temperature increases to about $1.5 \times 10^7 \text{ K}$, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star “ignites,” creating a yellow star like our sun.

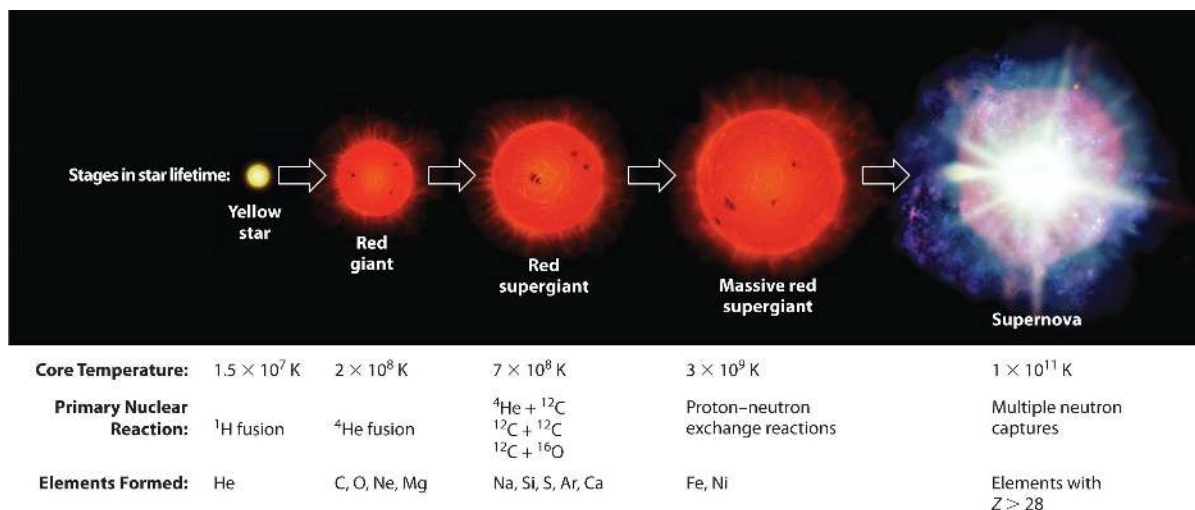


Figure 19.2.2: Nuclear Reactions during the Life Cycle of a Massive Star. At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to “burn,” undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

The stages in a star's lifetime are yellow star, red giant, red supergiant, massive red supergiant and finally supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:



The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

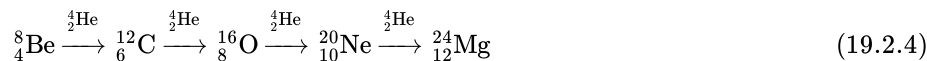


These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:



Although beryllium-8 has both an even mass number and an even atomic number, it also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

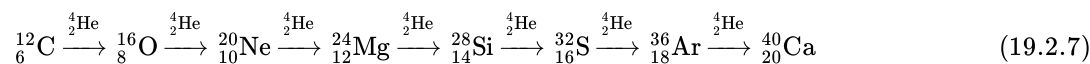


So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a red giant that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm³, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:



At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:



The energy released by these reactions causes a further expansion of the star to form a red supergiant, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with $Z > 28$. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called **supernovas** (Figure 19.2.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting neutron star is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or nebula (Figure 19.2.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β -decay processes to produce tin-120:

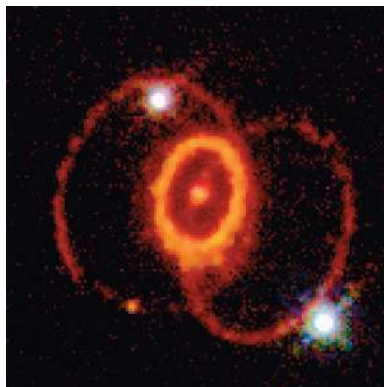
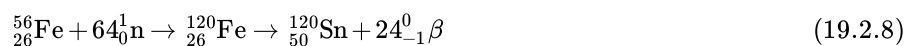


Figure 19.2.3: A Supernova. A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

✓ Example 19.2.1: Carbon Burning Stars

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

- magnesium-24.
- neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

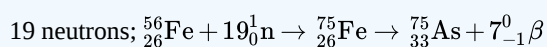
Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution

- a. A magnesium-24 nucleus ($Z = 12$, $A = 24$) has the same nucleons as two carbon-12 nuclei ($Z = 6$, $A = 12$). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: ${}^{12}_6\text{C} + {}^{12}_6\text{C} \rightarrow {}^{24}_{12}\text{Mg}$.
- b. The neon-20 product has $Z = 10$ and $A = 20$. The conservation of mass requires that the other product have $A = (2 \times 12) - 20 = 4$; because of conservation of charge, it must have $Z = (2 \times 6) - 10 = 2$. These are the characteristics of an α particle. The reaction is therefore ${}^{12}_6\text{C} + {}^{12}_6\text{C} \rightarrow {}^{20}_{10}\text{Ne} + {}^4_2\alpha$.

? Exercise 19.2.1

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer**Summary**

Hydrogen and helium are the most abundant elements in the universe. Heavier elements are formed in the interior of stars via multiple neutron-capture events. By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

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19.3: Kinetics of Radioactive Decay

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the **half-life** of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_{0/2}$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[A]_0}{[A]} = kt \quad (19.3.1)$$

Substituting $[A]_{0/2}$ for $[A]$ and $t_{1/2}$ for t (to indicate a half-life) into Equation 19.3.1 gives

$$\ln \frac{[A]_0}{[A]_{0/2}} = \ln 2 = kt_{1/2} \quad (19.3.2)$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \quad (19.3.3)$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 19.3.1, and is *independent* of $[A]$.

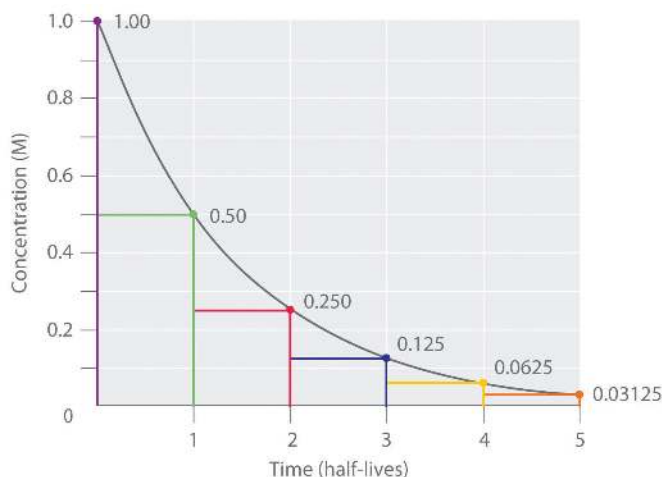


Figure 19.3.1: The Half-Life of a First-Order Reaction. This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$

Number of Half-Lives	Percentage of Reactant Remaining	
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2} \left(\frac{1}{2} \right) \left(\frac{1}{2} \right) (100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2} \right)^n (100\%) = \left(\frac{1}{2} \right)^n \%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of $[A]$.

✓ Example 19.3.1

The anticancer drug cis-platin hydrolyzes in water with a rate constant of $1.5 \times 10^{-3} \text{ min}^{-1}$ at pH 7.0 and 25°C . Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cis-platin has a concentration of 0.053 M, what will be the concentration of cis-platin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

- Use Equation 19.3.3 to calculate the half-life of the reaction.
- Multiply the initial concentration by $1/2$ to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.
- Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution A

We can calculate the half-life of the reaction using Equation 19.3.3

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3} \text{ min}^{-1}} = 4.6 \times 10^2 \text{ min}$$

Thus it takes almost 8 h for half of the cis-platin to hydrolyze.

Solution B

After 5 half-lives (about 38 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053 \text{ M}}{2^5} = \frac{0.053 \text{ M}}{32} = 0.0017 \text{ M}$$

After 10 half-lives (77 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053 \text{ M}}{2^{10}} = \frac{0.053 \text{ M}}{1024} = 5.2 \times 10^{-5} \text{ M}$$

Solution C

The percent completion after 5 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053 \text{ M} - 0.0017 \text{ M})(100)}{0.053} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053 \text{ M} - 5.2 \times 10^{-5} \text{ M})(100)}{0.053 \text{ M}} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

? Exercise 19.3.1

Ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6} \text{ s}^{-1}$ at 650°C .

- What is the half-life for the reaction under these conditions?
- If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C , what is the concentration of ethyl chloride after 4 half-lives?

Answer a

$$4.3 \times 10^5 \text{ s} = 120 \text{ h} = 5.0 \text{ days};$$

Answer b

$$4.8 \times 10^{-3} \text{ M}$$

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (A)** as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \quad (19.3.4)$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \quad (19.3.5)$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1} , yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 19.3.4 and Equation 19.3.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \quad (19.3.6)$$

Equation 19.3.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 19.3.6) or the integrated rate law:

$$N = N_0 e^{-kt} \quad (19.3.7)$$

$$\ln \frac{N}{N_0} = -kt \quad (19.3.8)$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

Table 19.3.2: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99m*	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Note

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}\text{CO}_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}\text{CO}_2$ molecules as well as nonradioactive $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:



The half-life for this reaction is 5700 ± 30 yr.

The $^{14}\text{C}/^{12}\text{C}$ ratio in living organisms is 1.3×10^{-12} , with a decay rate of 15 dpm/g of carbon (Figure 19.3.2). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11. Using this method implicitly assumes that the $^{14}\text{CO}_2/^{12}\text{CO}_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}\text{CO}_2/^{12}\text{CO}_2$ ratio over time.

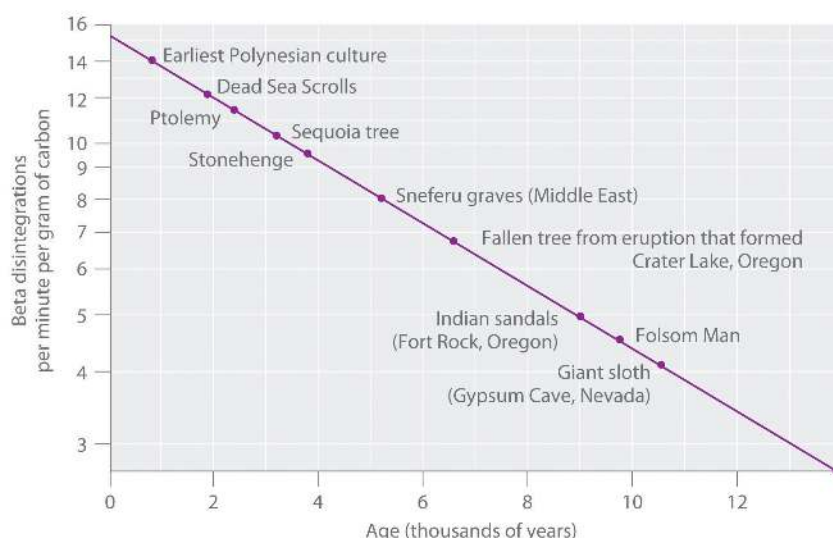


Figure 19.3.2: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

✓ Example 19.3.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy: Step A

Use Equation 19.3.5 to calculate N_0/N . Then substitute the value for the half-life of ^{14}C into Equation 19.3.3 to find the rate constant for the reaction.

Strategy: Step B

Using the values obtained for N_0/N and the rate constant, solve Equation 19.3.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 19.3.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt \quad (19.3.10)$$

$$\frac{\ln(N_0/N)}{k} = t \quad (19.3.11)$$

Step A

From Equation 19.3.5, we know that $A = kN$. We can therefore use the initial and final activities ($A_0 = 15$ dpm and $A = 8.0$ dpm) to calculate N_0/N :

$$\frac{A_0}{A} = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 19.3.3

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

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}} = 1.22 \times 10^{-4} \text{ yr}^{-1}$$

Step B

Substituting into the equation for t ,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4} \text{ yr}^{-1}} = 5.2 \times 10^3 \text{ yr}$$

From our calculations, the man died 5200 yr ago.

? Exercise 19.3.2

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

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19.4: Radiation in Biology and Medicine

Learning Objectives

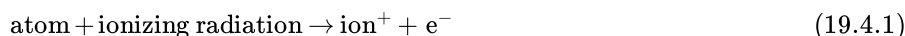
- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:



Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 19.4.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1 \text{ MeV/particle} = 96 \text{ billion J/mol.}$$



Figure 19.4.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 19.4.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

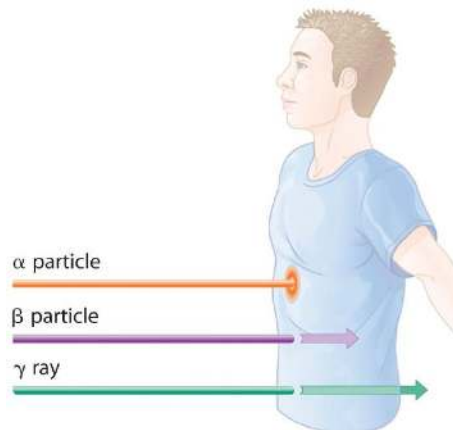


Figure 19.4.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 19.4.1.

Table 19.4.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$< 10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2} – 10^1	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure. Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \quad 1 \text{ Gy} = 1 \text{ J/kg} \quad (19.4.2)$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs $0.010 \text{ J}/70 \text{ kg} = 1.4 \times 10^{-4} \text{ J}$, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because

the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the **RBE** (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 19.4.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

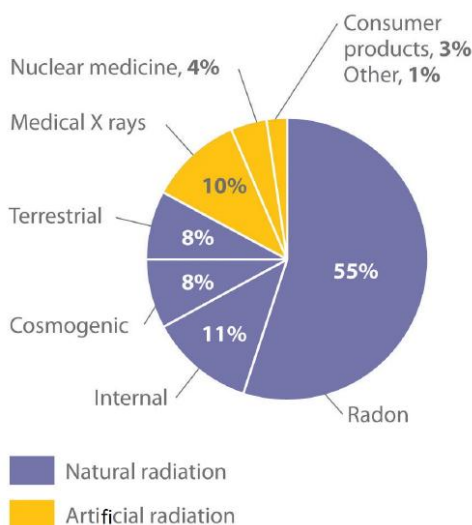


Figure 19.4.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C :



The carbon atoms react with oxygen atoms to form CO_2 , which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C , which decays by beta emission. About 5000

^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^3H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^3H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as ^{232}Th and ^{238}U as well as radioactive daughter isotopes, such as ^{226}Ra . The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% ^{40}K , which decays by emitting both a β particle and a (γ) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 ^{40}K nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of ^{238}U , and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb :



Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of ^{218}Po releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The ^{218}Po isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^3H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

✓ Example 19.4.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

- Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
- Determine the number of decays per year for this amount of ^{40}K .
- Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K :

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K , so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K} \times \frac{1.05 \times 10^7 \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned} \text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^6 \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr} \end{aligned}$$

We use the definition of the rad ($1 \text{ rad} = 10^{-2} \text{ J/kg}$ of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned} \text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr} \end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

? Exercise 19.4.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+} . Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr ?

Answer

$5.7 \times 10^3 \text{ rad/yr}$ (which is 10 times the fatal dose)

📌 Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 19.4.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 19.4.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 19.4.4 but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

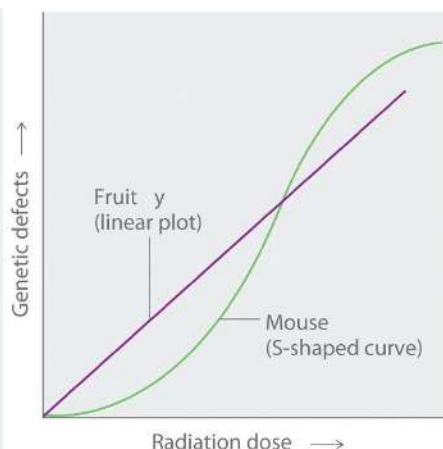


Figure 19.4.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

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19.5: Nuclear Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:



Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products ($118 + 132 + 4 = 254$) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [$46 + 52 + (4 \times 0) = 98$] is the same as the atomic number of the parent nuclide.

✓ Example 19.5.1

Write a balanced nuclear equation to describe each reaction.

- the beta decay of $^{35}_{16}\text{S}$
- the decay of $^{201}_{80}\text{Hg}$ by electron capture
- the decay of $^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of A and Z to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ^A_ZX :

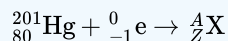


B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

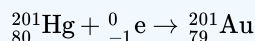


b.

A We know the identities of both reactants: $^{201}_{80}\text{Hg}$ and an inner electron, $^0_{-1}\text{e}$. The reaction is as follows:

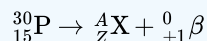


B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus



c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore



B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:



? Exercise 19.5.1

Write a balanced nuclear equation to describe each reaction.

- ${}_{6}^{11}\text{C}$ by positron emission
- the beta decay of molybdenum-99
- the emission of an α particle followed by gamma emission from ${}_{74}^{185}\text{W}$

Answer

- ${}_{6}^{11}\text{C} \rightarrow {}_{5}^{11}\text{B} + {}_{+1}^0\beta$
- ${}_{42}^{99}\text{Mo} \rightarrow {}_{43}^{99m}\text{Tc} + {}_{-1}^0\beta$
- ${}_{74}^{185}\text{W} \rightarrow {}_{72}^{181}\text{Hf} + {}_2^4\alpha + {}_0^0\gamma$

✓ Example 19.5.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

- ${}_{22}^{45}\text{Ti}$
- ${}_{94}^{242}\text{Pu}$
- ${}_{5}^{12}\text{B}$
- ${}_{100}^{256}\text{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of Z , predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

- This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
- Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus ${}_{94}^{242}\text{Pu}$ is expected to decay by alpha emission.
- This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that ${}_{5}^{12}\text{B}$ will undergo beta decay.
- This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that ${}_{100}^{256}\text{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

? Exercise 19.5.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

- ${}_{14}^{32}\text{Si}$

- b. $^{43}_{21}\text{Sc}$
- c. $^{231}_{91}\text{Pa}$

Answer

- a. beta decay
- b. positron emission or electron capture
- c. alpha decay

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19.6: Nuclear Fusion and Nucleosynthesis

Learning Objectives

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:



A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^4_2\text{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^2_1\text{H}$ and a triton, ${}^3_1\text{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:



This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^9 kilojoules per mole of ${}^4_2\text{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

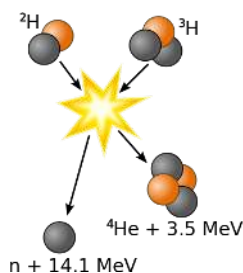


Figure 19.6.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)]

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 19.6.2).

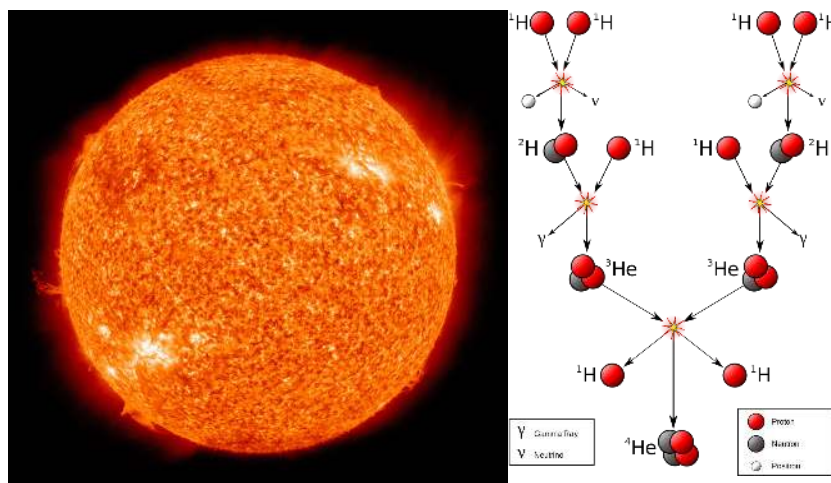


Figure 19.6.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

✓ Example 19.6.1

Calculate the energy released in each of the following hypothetical processes.

- $3\,{}^4_2\text{He} \rightarrow {}^{12}_6\text{C}$
- $6\,{}^1_1\text{H} + 6\,{}^1_0\text{n} \rightarrow {}^{12}_6\text{C}$
- $6\,{}^2_1\text{D} \rightarrow {}^{12}_6\text{C}$

Solution

- $Q_a = 3 \times 4.0026 - 12.0000\text{ amu} \times (1.4924 \times 10^{-10}\text{ J/amu}) = 1.17 \times 10^{-12}\text{ J}$
- $Q_b = (6 \times (1.007825 + 1.008665) - 12.000000)\text{ amu} \times (1.4924 \times 10^{-10}\text{ J/amu}) = 1.476 \times 10^{-11}\text{ J}$
- $Q_c = 6 \times 2.014102 - 12.000000\text{ amu} \times (1.4924 \times 10^{-10}\text{ J/amu}) = 1.263 \times 10^{-11}\text{ J}$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

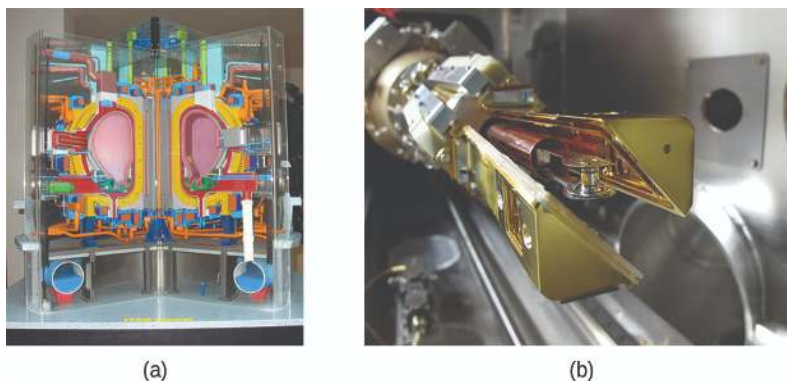


Figure 19.6.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 19.6.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a [Creative Commons Attribution License 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license. Download for free at <http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110>.

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CHAPTER OVERVIEW

UNIT II: ELECTRO-CHEMISTRY

UC Davis CHE 2CH Honors General Chemistry III

Unit I: Chemistry Fundamentals • Unit II: Bonding
Agenda • Homework Exercises • Worksheets

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. In this chapter, the married subjects of thermodynamics and equilibrium will be expanded to a troika by including electrochemistry. The ability to "steal" and "donate" electrons will be introduced and discussed in the context of free energies, enthalpies, entropies and equilibrium constants.

Topic hierarchy

- [17.1: Electrochemical Cells](#)
- [17.2: The Gibbs Free Energy and Cell Voltage](#)
- [17.3: Concentration Effects and the Nernst Equation](#)
- [17.4: Batteries and Fuel Cells](#)
- [17.5: Corrosion and Its Prevention](#)
- [17.6: Electrometallurgy](#)
- [17.7: A Deeper Look: Electrolysis of Water and Aqueous Solutions](#)

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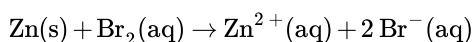
17.1: Electrochemical Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

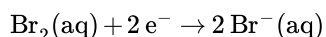
In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

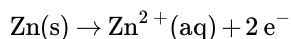


The half-reactions are as follows:

reduction half-reaction:



oxidation half-reaction:



Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and Br₂ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 17.1.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 17.1.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

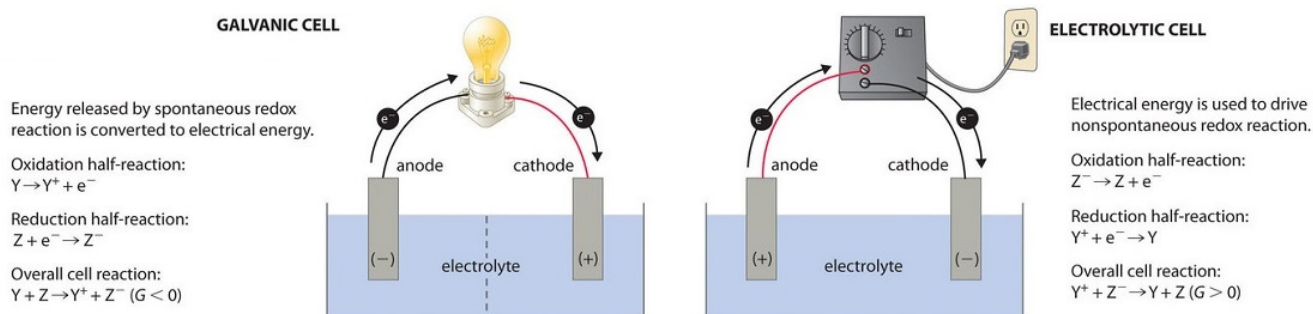
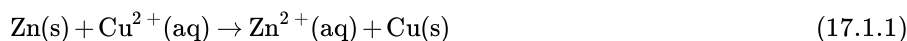


Figure 17.1.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:



We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure 17.1.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $\text{Zn}^{2+}(\text{aq})$ ions, while $\text{Cu}^{2+}(\text{aq})$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure 17.1.3a. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-} , respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the

circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 17.1.3b). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

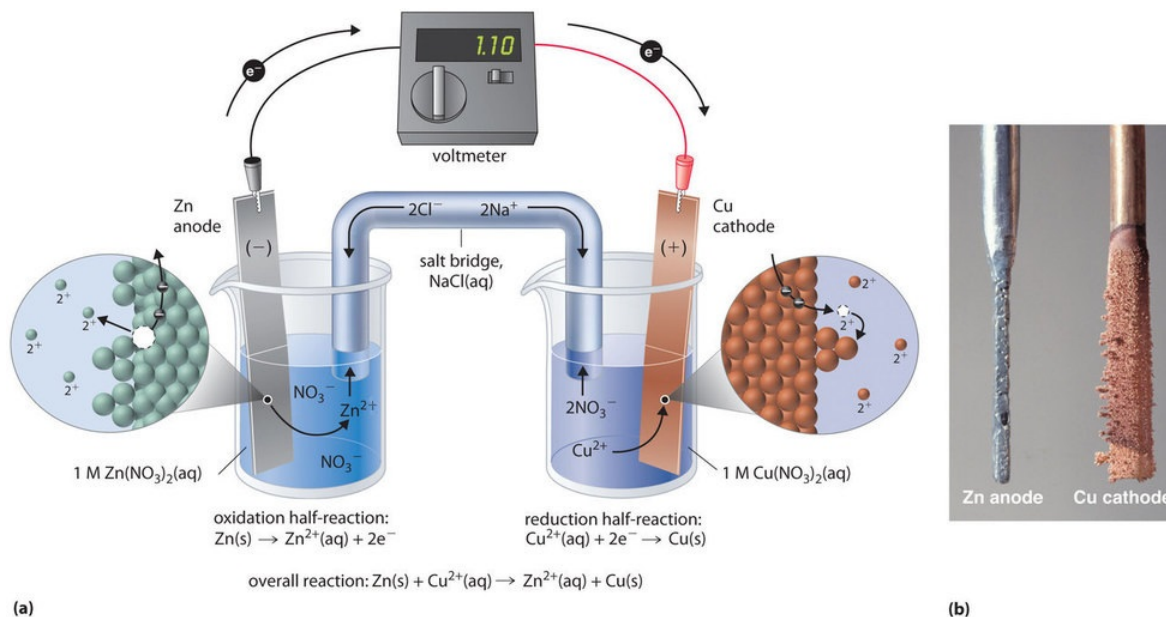


Figure 17.1.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $\text{Zn}^{2+}(\text{aq})$ ions, while the Cu cathode gains mass as $\text{Cu}^{2+}(\text{aq})$ ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

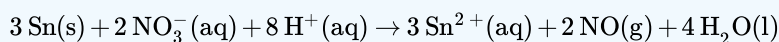
A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 17.1.3a). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 17.1.1.

A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.

✓ Example 17.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:



For this galvanic cell,

- write the half-reaction that occurs at each electrode.
- indicate which electrode is the cathode and which is the anode.
- indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

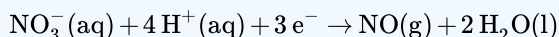
Strategy:

- Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
- From the direction of electron flow, assign each electrode as either positive or negative.

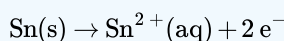
Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2 , with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:



oxidation:



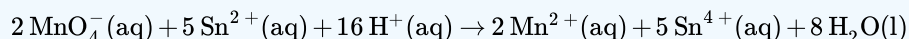
Thus nitrate is reduced to NO , while the tin electrode is oxidized to Sn^{2+} .

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

? Exercise 17.1.1

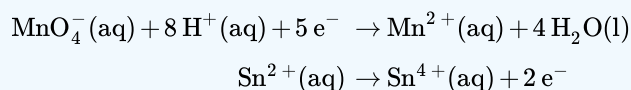
Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:



For this galvanic cell,

- write the half-reaction that occurs at each electrode.
- indicate which electrode is the cathode and which is the anode.
- indicate which electrode is positive and which is negative.

Answer a



Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.



Electrochemical Cells: [Electrochemical Cells](#)(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in Figure 17.1.3a is written as follows:

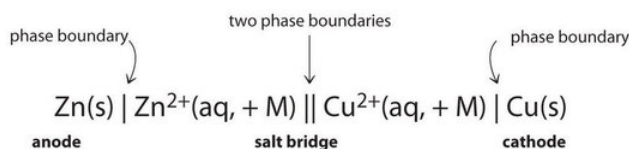
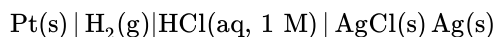


Figure 17.1.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

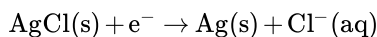
At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

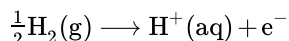


This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

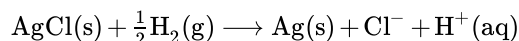
cathode reaction:



anode reaction:



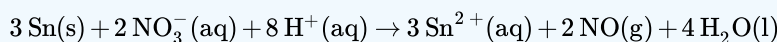
overall:



A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

✓ Example 17.1.2

Draw a cell diagram for the galvanic cell described in Example 17.1.1. The balanced chemical reaction is as follows:



Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

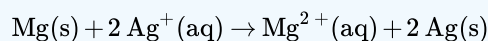
The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\text{Sn(s)} | \text{Sn}^{2+}(\text{aq})$. We could include $\text{H}_2\text{SO}_4(\text{aq})$ with the contents of the anode compartment, but the sulfate ion (as HSO_4^-) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\text{HNO}_3(\text{aq}) | \text{NO(g)} | \text{Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,



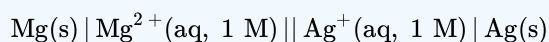
The solution concentrations were not specified, so they are not included in this cell diagram.

? Exercise 17.1.2

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:



Answer





Cell Diagrams: [Cell Diagrams](#)(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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17.2: The Gibbs Free Energy and Cell Voltage

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

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 $\text{Ni}^{2+}(\text{aq})$ to form Ni(s) and $\text{Co}^{2+}(\text{aq})$ occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that $[\text{Ni}^{2+}]$ 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 & Gibbs 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 ($1 \text{ C} = 1 \text{ A} \cdot \text{s}$):

$$\frac{1 \text{ J}}{1 \text{ V}} = 1 \text{ C} = \text{A} \cdot \text{s}$$

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):

$$\begin{aligned} F &= (1.60218 \times 10^{-19} \text{ C}) \left(\frac{6.02214 \times 10^{23} \text{ J}}{1 \text{ mol e}^-} \right) \\ &= 9.64833212 \times 10^4 \text{ C/mol e}^- \\ &\simeq 96,485 \text{ J/(V} \cdot \text{mol e}^-) \end{aligned}$$

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):

$$w_{\text{max}} = nFE_{\text{cell}}$$

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 ($\Delta G = w_{\text{max}}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG ; this

relationship is as follows:

$$\Delta G = -nFE_{\text{cell}}$$

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:

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad (17.2.1)$$

A spontaneous redox reaction is characterized by a negative value of ΔG° , which corresponds to a positive value of E_{cell}° .

✓ Example 17.2.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in [Table P2](#), calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG° for the reaction and spontaneity

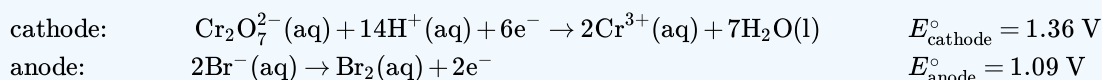
Strategy:

- From the relevant half-reactions and the corresponding values of E° , write the overall reaction and calculate E_{cell}° .
- Determine the number of electrons transferred in the overall reaction. Then use Equation 17.2.1 to calculate ΔG° . If ΔG° is negative, then the reaction is spontaneous.

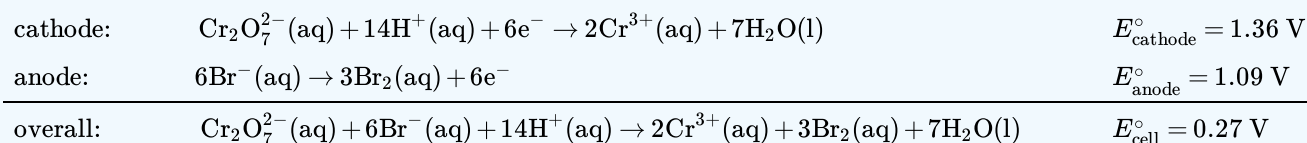
Solution

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° . From [Table P2](#), we can find the reduction and oxidation half-reactions and corresponding E° values:



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:



B

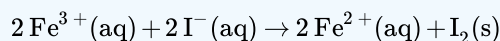
We can now calculate ΔG° using Equation 17.2.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}
 \Delta G^{\circ} &= -(n)(F)(E_{\text{cell}}^{\circ}) \\
 &= -(6 \text{ mole})[96,485 \text{ J}/(\text{V} \cdot \text{mol})(0.27 \text{ V})] \\
 &= -15.6 \times 10^4 \text{ J} \\
 &= -156 \text{ kJ/mol Cr}_2\text{O}_7^{2-}
 \end{aligned}$$

Thus ΔG° is -168 kJ/mol for the reaction as written, and the reaction is spontaneous.

? Exercise 17.2.1

Use the data in [Table P2](#) to calculate ΔG° for the reduction of ferric ion by iodide:



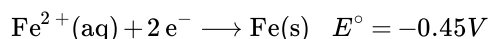
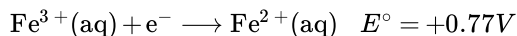
Is the reaction spontaneous?

Answer

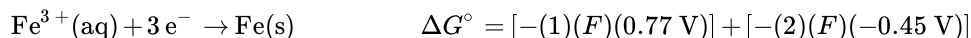
−44 kJ/mol I₂; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of Fe³⁺(aq) to Fe(s) is not listed in the table, but two related reductions are given:



Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E° is not a state function. However, because ΔG° is a state function, the sum of the ΔG° values for the individual reactions gives us ΔG° for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E° for the overall half-reaction, we first must add the values of $\Delta G^{\circ} (= -nFE^{\circ})$ for each individual half-reaction to obtain ΔG° for the overall half-reaction:



Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^{\circ} = F[(-0.77\text{V}) + (-2)(-0.45\text{V})] = F(0.13\text{V})$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 17.2.1 and solving for E° gives the following:

$$\begin{aligned} \Delta G^{\circ} &= -nFE_{\text{cell}}^{\circ} \\ F(0.13\text{ V}) &= -(3)(F)(E_{\text{cell}}^{\circ}) \\ E^{\circ} &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V} \end{aligned}$$

This value of E° is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

Values of E° for half-reactions cannot be added to give E° for the sum of the half-reactions; only values of $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ for half-reactions can be added.

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K , to obtain a relationship between E_{cell}° and K . Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^{\circ} = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 17.2.1), we can write

$$-nFE_{\text{cell}}^{\circ} = -RT \ln K$$

Rearranging this equation,

$$E_{\text{cell}}^{\circ} = \left(\frac{RT}{nF} \right) \ln K \quad (17.2.2)$$

For $T = 298 \text{ K}$, Equation 17.2.2 can be simplified as follows:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= \left(\frac{RT}{nF} \right) \ln K \\ &= \left[\frac{[8.314 \text{ J}/(\text{mol} \cdot \text{K})(298 \text{ K})]}{n[96,485 \text{ J}/(\text{V} \cdot \text{mol})]} \right] 2.303 \log K \\ &= \left(\frac{0.0592 \text{ V}}{n} \right) \log K \end{aligned} \quad (17.2.3)$$

Thus E_{cell}° is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E_{cell}° and vice versa.

✓ Example 17.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give PbSO_4 under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

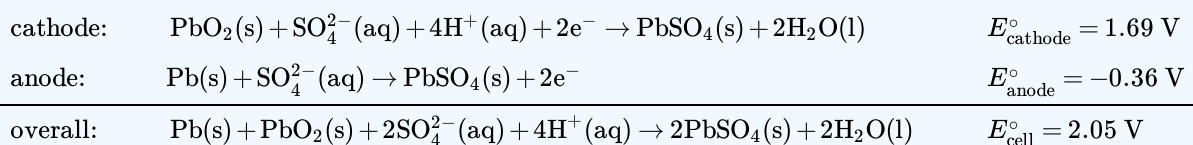
Asked for: K

Strategy:

- Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E_{cell}° .
- Determine the number of electrons transferred in the overall reaction. Use Equation 17.2.3 to solve for $\log K$ and then K .

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:



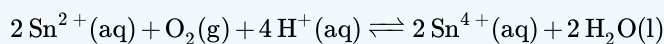
B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 17.2.3 for $\log K$ and inserting the values of n and E° ,

$$\begin{aligned} \log K &= \frac{nE^{\circ}}{0.0591 \text{ V}} = \frac{2(2.05 \text{ V})}{0.0591 \text{ V}} = 69.37 \\ K &= 2.3 \times 10^{69} \end{aligned}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

? Exercise 17.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}(\text{aq})$ with oxygen to produce $\text{Sn}^{4+}(\text{aq})$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:



Answer

$$5.7 \times 10^{72}$$

Figure 17.2.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q .

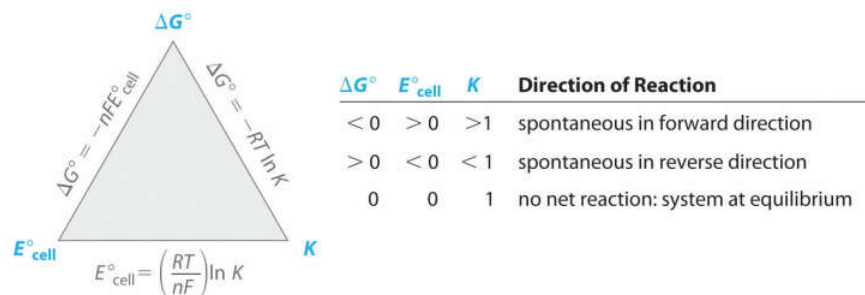


Figure 17.2.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K , ΔG° , and E°_{cell} . If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and E°_{cell} and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E° is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E° is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium.

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell} . Because the equilibrium constant K is related to ΔG , E°_{cell} and K are also related. Large equilibrium constants correspond to large positive values of E° .

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17.3: Concentration Effects and the Nernst Equation

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the [reaction quotient](#) and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG , is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (17.3.1)$$

We also know that $\Delta G = -nFE_{\text{cell}}$ (under non-standard conditions) and $\Delta G^\circ = -nFE_{\text{cell}}^\circ$ (under standard conditions). Substituting these expressions into Equation [17.3.1](#), we obtain

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q \quad (17.3.2)$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left(\frac{RT}{nF} \right) \ln Q \quad (17.3.3)$$

Equation [17.3.3](#) is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation [17.3.3](#) reduces to Equation [17.3.4](#) and [17.3.5](#) because $Q = K$, and there is no net transfer of electrons (i.e., $E_{\text{cell}} = 0$).

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left(\frac{RT}{nF} \right) \ln K = 0 \quad (17.3.4)$$

since

$$E_{\text{cell}}^\circ = \left(\frac{RT}{nF} \right) \ln K \quad (17.3.5)$$

Substituting the values of the constants into Equation [17.3.3](#) with $T = 298 \text{ K}$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential (E_{cell}°), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q \quad (17.3.6)$$

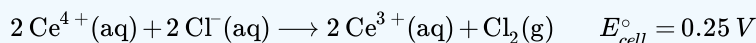
The Power of the Nernst Equation

The Nernst Equation ([17.3.3](#)) can be used to determine the value of E_{cell} , and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation [17.3.6](#) allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation [17.3.6](#) that the cell potential changes by $0.0591/n \text{ V}$ for each 10-fold change in the value of Q because $\log 10 = 1$.

✓ Example 17.3.1

The following reaction proceeds spontaneously under standard conditions because $E^\circ_{\text{cell}} > 0$ (which means that $\Delta G^\circ < 0$):



Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[\text{Ce}^{4+}] = 0.013 \text{ M}$, $[\text{Ce}^{3+}] = 0.60 \text{ M}$, $[\text{Cl}^{-}] = 0.0030 \text{ M}$, $P_{\text{Cl}_2} = 1.0 \text{ atm}$, and $T = 25^\circ\text{C}$.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

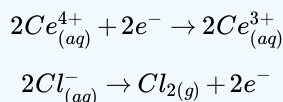
Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell} . Moreover, because the temperature is 25°C (298 K), we can use Equation 17.3.6 instead of Equation 17.3.3. The overall reaction involves the net transfer of two electrons:



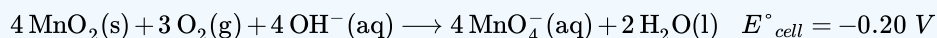
so $n = 2$. Substituting the concentrations given in the problem, the partial pressure of Cl_2 , and the value of E°_{cell} into Equation 17.3.6,

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q \\ &= 0.25 \text{ V} - \left(\frac{0.0591 \text{ V}}{2} \right) \log \left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2 [\text{Cl}^{-}]^2} \right) \\ &= 0.25 \text{ V} - [(0.0296 \text{ V})(8.37)] = 0.00 \text{ V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because $E = 0 \text{ V}$ and $\Delta G = 0$). The composition specified is that of an equilibrium mixture

? Exercise 17.3.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

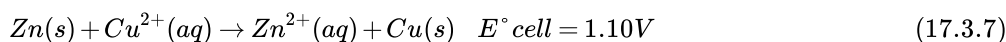


Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: $\text{pH } 10$, $P_{\text{O}_2} = 0.20 \text{ atm}$, $[\text{MnO}_4^{-}] = 1.0 \times 10^{-4} \text{ M}$, and $T = 25^\circ\text{C}$.

Answer

$E_{\text{cell}} = -0.22 \text{ V}$; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:



The reaction quotient is therefore $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and $1.0 \times 10^{-6} \text{ M Zn}^{2+}$. The initial voltage measured when the cell is connected can then be calculated from Equation 17.3.6

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{0.0591 \text{ V}}{n} \right) \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (17.3.8)$$

$$= 1.10 \text{ V} - \left(\frac{0.0591 \text{ V}}{2} \right) \log \left(\frac{1.0 \times 10^{-6}}{1.0} \right) = 1.28 \text{ V} \quad (17.3.9)$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[\text{Zn}^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[\text{Cu}^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, so $Q = 1$ and $E_{\text{cell}} = E_{\text{cell}}^{\circ}$. Beyond this point, $[\text{Zn}^{2+}]$ will continue to increase in the anode compartment, and $[\text{Cu}^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell} . When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and $1.0 \times 10^{-6} \text{ M Cu}^{2+}$), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V .

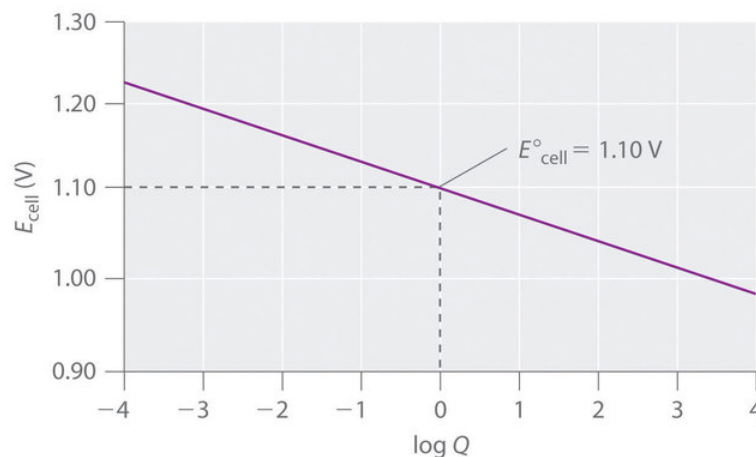


Figure 17.3.1: The Variation of E_{cell} with $\log Q$ for a Zn/Cu Cell. Initially, $\log Q < 0$, and the voltage of the cell is greater than E_{cell}° . As the reaction progresses, $\log Q$ increases, and E_{cell} decreases. When $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, $\log Q = 0$ and $E_{\text{cell}} = E_{\text{cell}}^{\circ} = 1.10 \text{ V}$. As long as the electrical circuit remains intact, the reaction will continue, and $\log Q$ will increase until $Q = K$ and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of $-0.0591/n$, as illustrated in Figure 17.3.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is “dead.” The value of Q when $E_{\text{cell}} = 0$ is calculated as follows:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q = 0 \quad (17.3.10)$$

$$E^{\circ} = \left(\frac{0.0591 \text{ V}}{n} \right) \log Q \quad (17.3.11)$$

$$\log Q = \frac{E^{\circ} n}{0.0591 \text{ V}} = \frac{(1.10 \text{ V})(2)}{0.0591 \text{ V}} = 37.23 \quad (17.3.12)$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \quad (17.3.13)$$

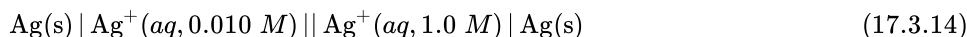
Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C .



The Nernst Equation: [The Nernst Equation \(opens in new window\)](#) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M AgNO_3 in one compartment and 1.0 M AgNO_3 in the other. The cell diagram and corresponding half-reactions are as follows:



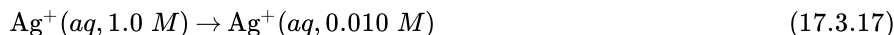
cathode:



anode:



Overall



As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of Ag(s) in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for E°_{cell} because $E^\circ_{\text{cathode}} = -E^\circ_{\text{anode}}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q \\ &= 0 - \left(\frac{0.0591 \text{ V}}{1} \right) \log \left(\frac{0.010}{1.0} \right) \\ &= 0.12 \text{ V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell} . Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{\text{cell}} = 0$).

✓ Example 17.3.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of MnCl_2 as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of MnSO_4 as the anode ($T = 25^\circ\text{C}$).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

- Write the overall reaction that occurs in the cell.
- Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:



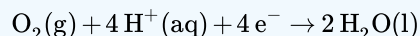
B For the reduction of $\text{Mn}^{2+}(\text{aq})$ to $\text{Mn}(\text{s})$, $n = 2$. We substitute this value and the given Mn^{2+} concentrations into Equation 17.3.6

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \left(\frac{0.0591\text{ V}}{n} \right) \log Q \\ &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{2} \right) \log \left(\frac{5.2 \times 10^{-2}}{2.0} \right) \\ &= 0.047\text{ V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 17.3.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with $P_{\text{O}_2} = 0.20\text{ atm}$. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:



What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30} . Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

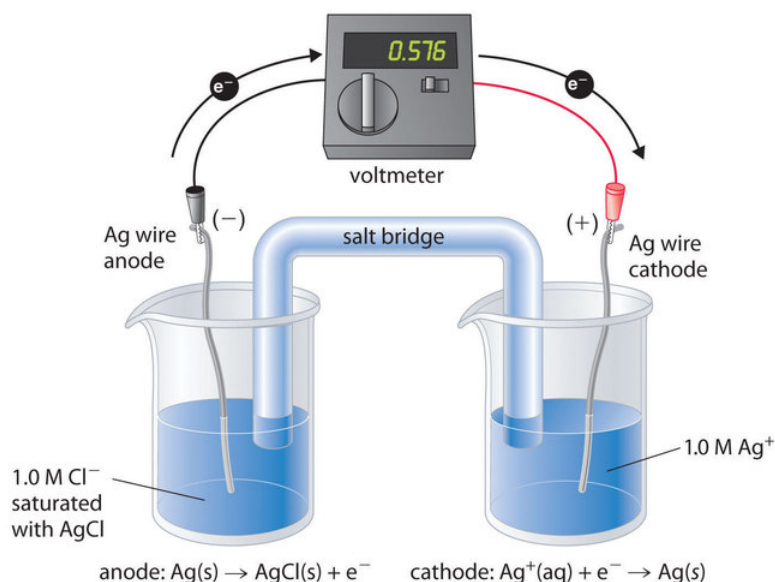


Figure 17.3.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+ , and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[\text{Ag}^+]$ between the two cells can be used to determine K_{sp} . (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 17.3.1, which is designed to measure the solubility product of silver chloride:

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

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+ ; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp} . We can see this by dividing both sides of the equation for K_{sp} by $[\text{Cl}^-]$ and substituting:

$$\begin{aligned} [\text{Ag}^+] &= \frac{K_{sp}}{[\text{Cl}^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}. \end{aligned}$$

The overall cell reaction is as follows:



Thus the voltage of the concentration cell due to the difference in $[\text{Ag}^+]$ between the two cells is as follows:

$$\begin{aligned} E_{\text{cell}} &= 0 \text{ V} - \left(\frac{0.0591 \text{ V}}{1} \right) \log \left(\frac{[\text{Ag}^+]_{\text{dilute}}}{[\text{Ag}^+]_{\text{concentrated}}} \right) \\ &= -0.0591 \text{ V} \log \left(\frac{K_{sp}}{1.0} \right) \\ &= -0.0591 \text{ V} \log K_{sp} \end{aligned} \tag{17.3.18}$$

By closing the circuit, we can measure the potential caused by the difference in $[\text{Ag}^+]$ in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 17.3.18 for K_{sp} ,

$$\begin{aligned} \log K_{sp} &= \frac{-E_{\text{cell}}}{0.0591 \text{ V}} = \frac{-0.580 \text{ V}}{0.0591 \text{ V}} = -9.81 \\ K_{sp} &= 1.5 \times 10^{-10} \end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

✓ Example 17.3.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate (PbSO_4) at 25°C , you construct a galvanic cell like the one shown in Figure 17.3.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with PbSO_4 in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for PbSO_4 ? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

- From the information given, write the equation for K_{sp} . Express this equation in terms of the concentration of Pb^{2+} .
- Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp} .

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4 . As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp} :

$$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$$

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{K_{\text{sp}}}{1.0 \text{ M}} = K_{\text{sp}}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:



so

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{0.0591}{n} \right) \log Q$$

$$0.230 \text{ V} = 0 \text{ V} - \left(\frac{0.0591 \text{ V}}{2} \right) \log \left(\frac{[\text{Pb}^{2+}]_{\text{dilute}}}{[\text{Pb}^{2+}]_{\text{concentrated}}} \right) = -0.0296 \text{ V} \log \left(\frac{K_{\text{sp}}}{1.0} \right)$$

$$-7.77 = \log K_{\text{sp}}$$

$$1.7 \times 10^{-8} = K_{\text{sp}}$$

? Exercise 17.3.3

A concentration cell similar to the one described in Example 17.3.3 contains a 1.0 M solution of lanthanum nitrate [$\text{La}(\text{NO}_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3 ? Report your answer to two significant figures.

Answer

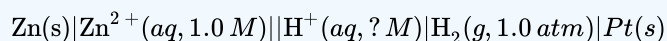
$$5.7 \times 10^{-17}$$

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 17.3.3 in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp} . Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[\text{H}^+]$ using a pH meter, as illustrated below.

✓ Example 17.3.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn²⁺ couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but [H⁺] in the second compartment is unknown. The cell diagram is as follows:



What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

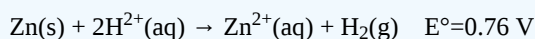
Asked for: pH of the solution

Strategy:

- Write the overall cell reaction.
- Substitute appropriate values into the Nernst equation and solve for $-\log[\text{H}^{+}]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H₂ (note that Zn lies below H₂ in [Table P2](#)):



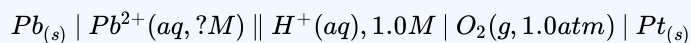
B By substituting the given values into the simplified Nernst equation (Equation [17.3.6](#)), we can calculate [H⁺] under nonstandard conditions:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \left(\frac{0.0591 \text{ V}}{n} \right) \log \left(\frac{[\text{Zn}^{2+}] P_{\text{H}_2}}{[\text{H}^{+}]^2} \right) \\ 0.26 \text{ V} &= 0.76 \text{ V} - \left(\frac{0.0591 \text{ V}}{2} \right) \log \left(\frac{(1.0)(1.0)}{[\text{H}^{+}]^2} \right) \\ 16.9 &= \log \left(\frac{1}{[\text{H}^{+}]^2} \right) = \log[\text{H}^{+}]^{-2} = (-2) \log[\text{H}^{+}] \\ 8.46 &= -\log[\text{H}^{+}] \\ 8.5 &= \text{pH} \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

? Exercise 17.3.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb²⁺ in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E^{\circ}_{\text{cathode}} = 1.23 \text{ V}$). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:



When the circuit is closed, the cell has a measured potential of 1.62 V. Use [Table P2](#) to determine the concentration of Pb²⁺ in the groundwater.

Answer

$$1.2 \times 10^{-9} M$$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical

except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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17.4: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 17.4.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (–) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

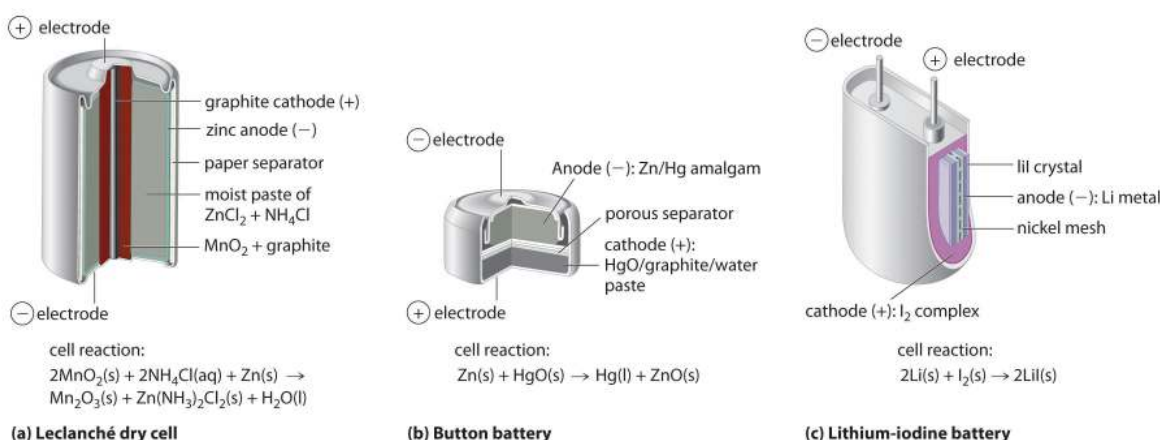


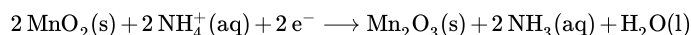
Figure 17.4.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a “wet cell,” in which the electrolyte is an acidic water-based paste containing MnO_2 , NH_4Cl , ZnCl_2 , graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2 . The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

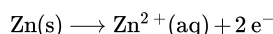
Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a “wet cell”: the electrolyte is an acidic water-based paste containing MnO_2 , NH_4Cl , ZnCl_2 , graphite, and starch (part (a) in Figure 17.4.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

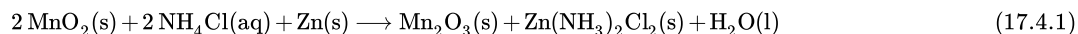


- anode (oxidation):

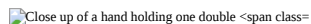


The Zn^{2+} ions formed by the oxidation of Zn(s) at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:



The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



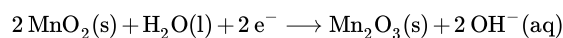
AA

battery" style="width: 287px; height: 215px;" width="287px" height="215px" data-cke-saved-src="/@api/deki/files/16647/battery.jpg" src="/@api/deki/files/16647/battery.jpg" data-quail-id="34">

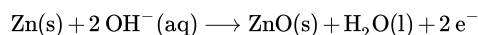
Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

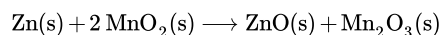
- cathode (reduction)



- anode (oxidation):



- overall reaction:



This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

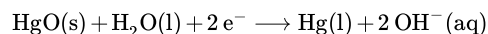
Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 17.4.1b.



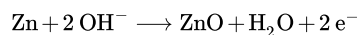
Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

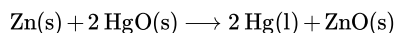
- cathode (mercury battery):



- Anode (mercury battery):

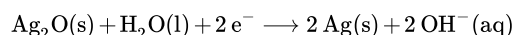


- overall reaction (mercury battery):

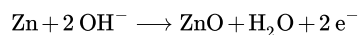


with $E_{\text{cell}} = 1.35 \text{ V}$.

- cathode reaction (silver battery):



- anode (silver battery):



- Overall reaction (silver battery):



with $E_{\text{cell}} = 1.6 \text{ V}$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually “dry.” They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2 . Separating them is a layer of solid LiI , which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):



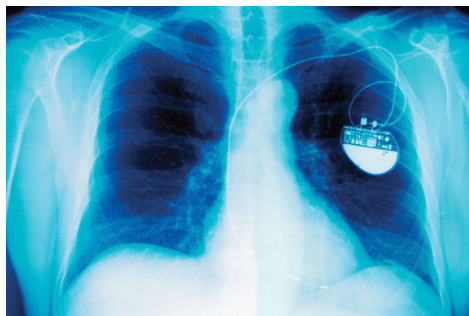
- anode (oxidation):



- overall:



with $E_{\text{cell}} = 3.5 \text{ V}$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure 17.4.1, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2 , for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH) . As shown in Figure 17.4.2 the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

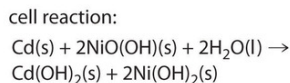
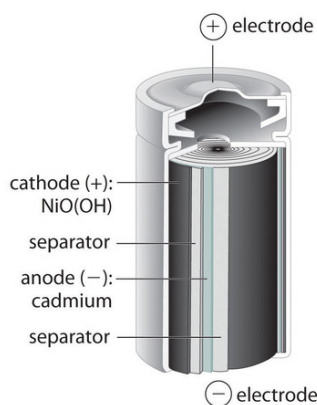
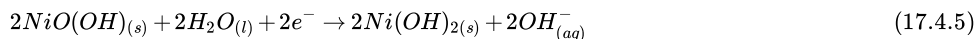


Figure 17.4.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a *NiCad* battery are as follows:

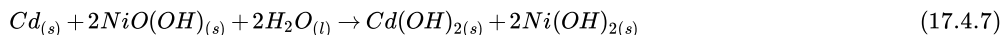
- cathode (reduction):



- anode (oxidation):



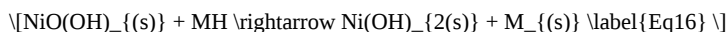
- overall:



$$E_{\text{cell}} = 1.4\text{V}$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [Cd(OH)_2 and 2Ni(OH)_2], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

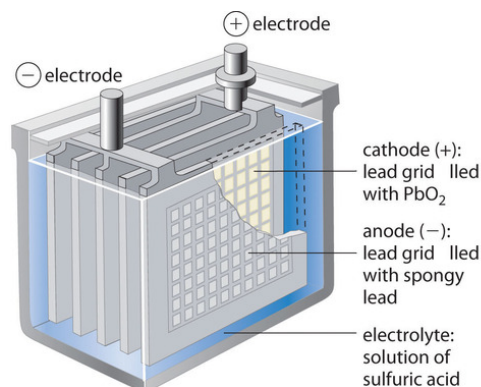


The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell (E°_{cell}) times the number of cells.



cell reaction:

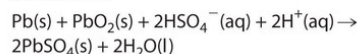
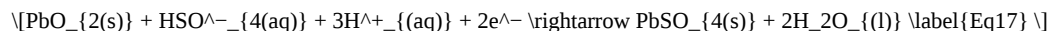


Figure 17.4.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure 17.4.3 the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):



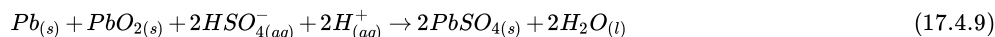
with $E^\circ_{\text{cathode}} = 1.685 \text{ V}$

- anode (oxidation):



with $E^\circ_{\text{anode}} = -0.356 \text{ V}$

- overall:



and $E^\circ_{\text{cell}} = 2.041 \text{ V}$

As the cell is discharged, a powder of PbSO_4 forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2 . If the battery is recharged too vigorously, however, [electrolysis](#) of water can occur:



This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

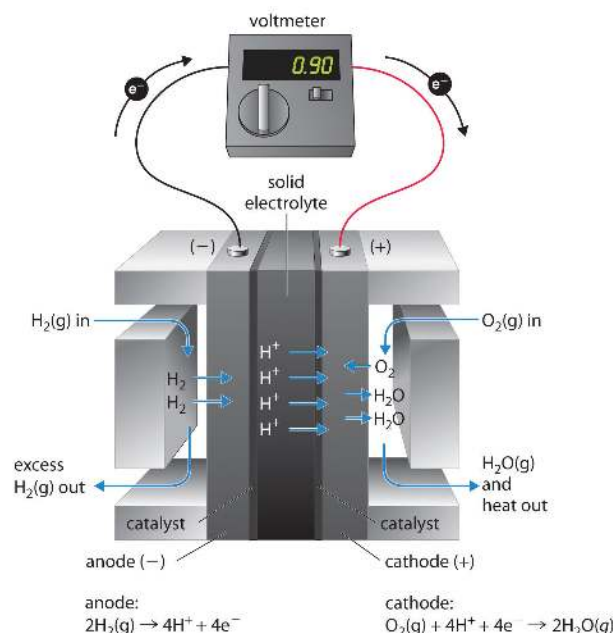


Figure 17.4.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 17.4.4. The electrode reactions are as follows:

- cathode (reduction):



- anode (oxidation):



- overall:



The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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17.5: Corrosion and Its Prevention

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated \$100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Corrosion is a REDOX process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), commonly known as rust, that does not provide a tight protective film (Figure 17.5.1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

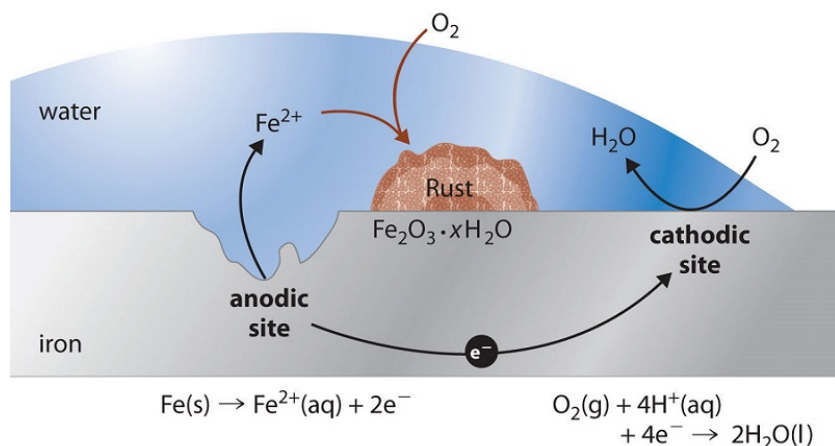
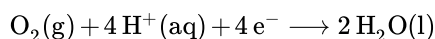


Figure 17.5.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $\text{Fe}^{2+}(\text{aq})$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

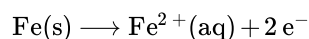
In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+} ; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:



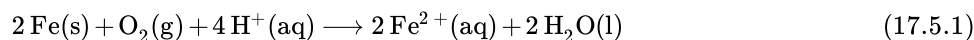
with $E_{\text{SRP}}^\circ = 1.23 \text{ V}$.

- at anode:



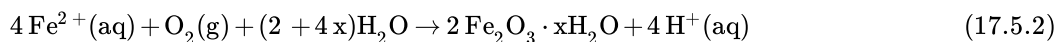
with $E_{SRP}^{\circ} = -0.45\text{ V}$.

- overall:



with $E_{cell}^{\circ} = 1.68\text{ V}$.

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+} , as represented in the following equation:



The sign and magnitude of E_{cell}° for the corrosion process (Equation 17.5.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^{+}). Under neutral conditions, the driving force is somewhat less but still appreciable ($E = 1.25\text{ V}$ at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^{+} and HCO_3^{-} provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 17.5.2).

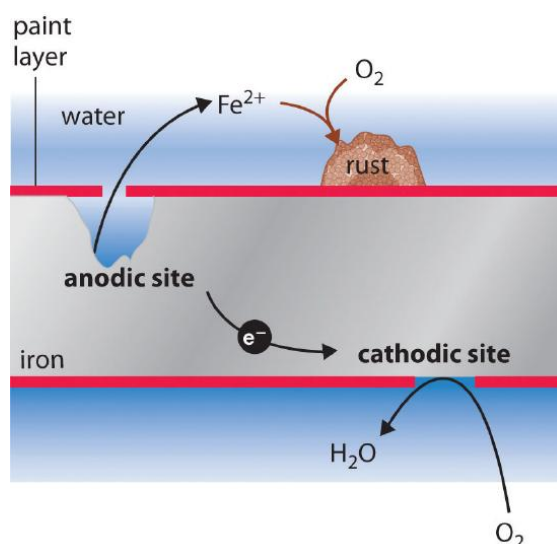


Figure 17.5.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to $\text{Fe}^{2+}(\text{aq})$ at the less exposed site (the anode). Rust is formed when $\text{Fe}^{2+}(\text{aq})$ diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the “tin cans” that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

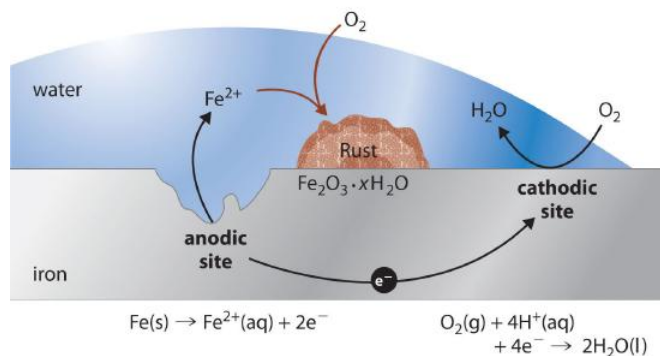
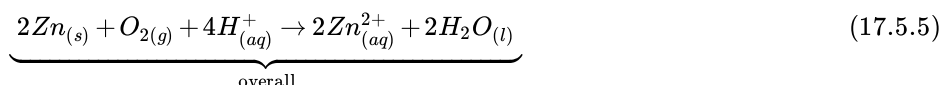


Figure 17.5.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn²⁺ ($E^\circ = -0.14$ V) and Fe²⁺ ($E^\circ = -0.45$ V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 17.5.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn ($E^\circ = -0.76$ V for $\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:



The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 17.5.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

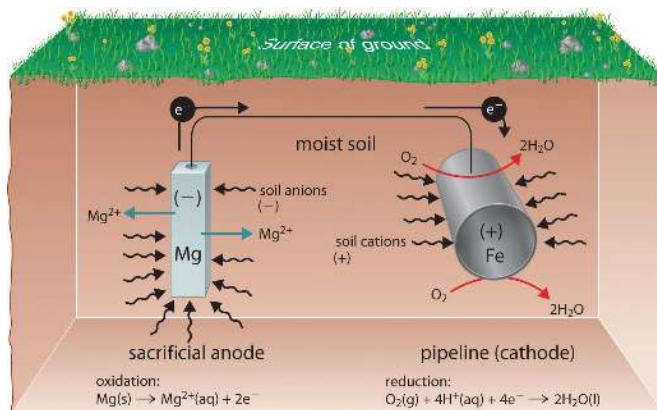


Figure 17.5.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E^\circ = -2.37 \text{ V}$) is much more easily oxidized than iron ($E^\circ = -0.45 \text{ V}$), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+ , diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

✓ Example 17.5.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

- If the boat is immersed in seawater, what corrosion reaction will occur? What is E°_{cell} ?
- How could you prevent this corrosion from occurring?

Given: identity of metals

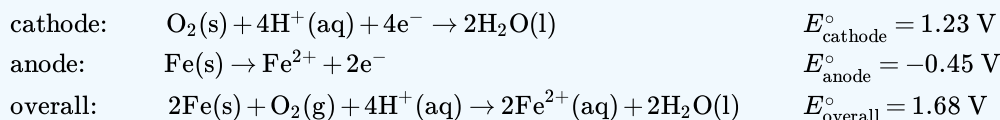
Asked for: corrosion reaction, E°_{cell} , and preventive measures

Strategy:

- Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate E°_{cell} .
- Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

- A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of E°_{cell} than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:



Over time, the iron screws will dissolve, and the boat will fall apart.

- B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 17.5.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 17.5.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

- Do you accept his proposal?
- What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer b

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2 , promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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17.6: Electrometallurgy

23.4: Electrometallurgy

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17.7: A Deeper Look: Electrolysis of Water and Aqueous Solutions

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 M Cd^{2+} solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure 17.7.1a).

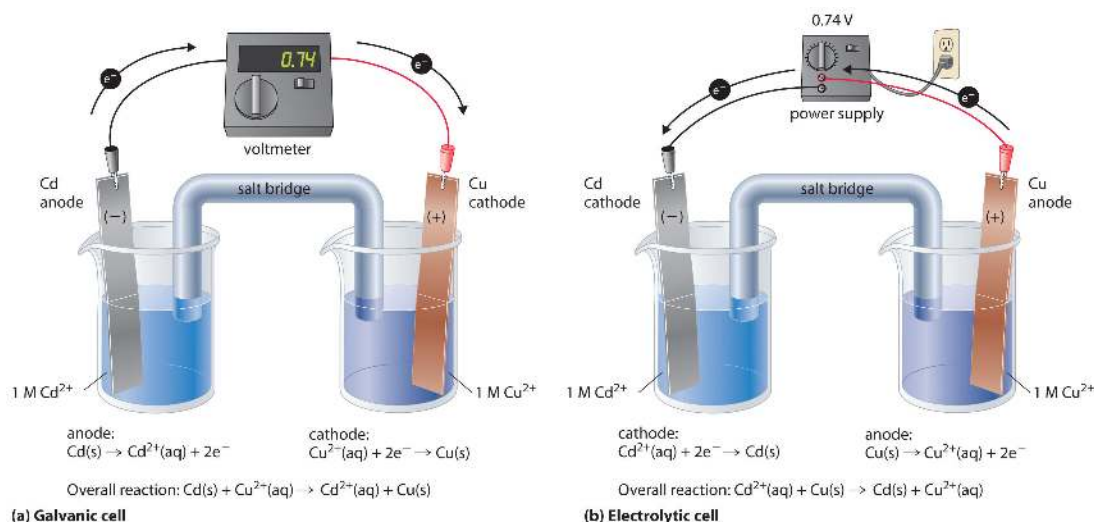
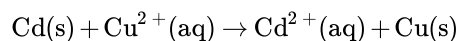


Figure 17.7.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M $\text{Cd}^{2+}(\text{aq})$ and a Cu electrode immersed in 1 M $\text{Cu}^{2+}(\text{aq})$ are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to $\text{Cd}^{2+}(\text{aq})$ at the anode, and $\text{Cu}^{2+}(\text{aq})$ is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to $\text{Cu}^{2+}(\text{aq})$] and into the Cd electrode [which is now the cathode, at which $\text{Cd}^{2+}(\text{aq})$ is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:



with $E^\circ_{\text{cell}} = 0.74 \text{ V}$

This reaction is thermodynamically spontaneous as written ($\Delta G^\circ < 0$):

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -(2 \text{ mol e}^-)[96,485 \text{ J/(V} \cdot \text{mol)}](0.74 \text{ V}) \\ &= -140 \text{ kJ (per mole Cd)} \end{aligned}$$

In this direction, the system is acting as a galvanic cell.

In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 17.7.1b). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:



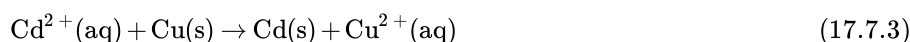
with $E_{\text{cathode}}^{\circ} = -0.40\text{ V}$

- half-reaction at the anode:



with $E_{\text{anode}}^{\circ} = 0.34\text{ V}$

- Overall Reaction:



with $E_{\text{cell}}^{\circ} = -0.74\text{ V}$

Because $E_{\text{cell}}^{\circ} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 17.7.1.

Table 17.7.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	–	+
cathode	+	–

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^{-} is oxidized at the anode, and Na^{+} is reduced at the cathode. The overall reaction is as follows:



This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C , well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a Downs cell (Figure 17.7.2). In this specialized cell, CaCl_2 (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C , thereby lowering operating costs.

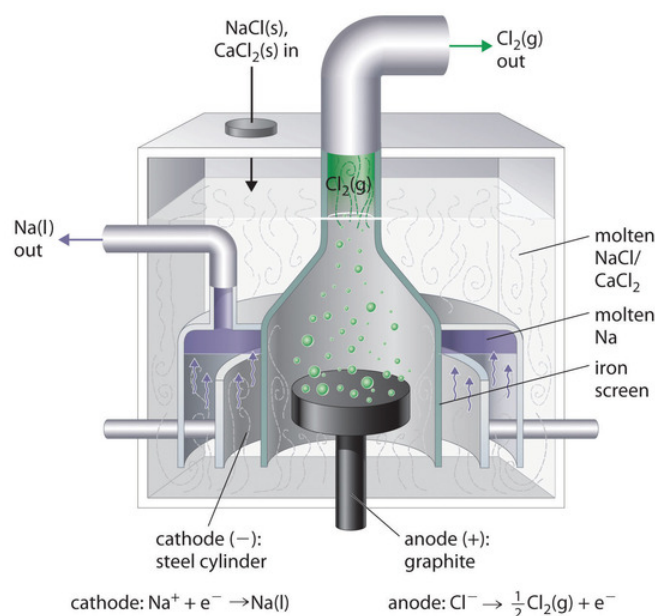
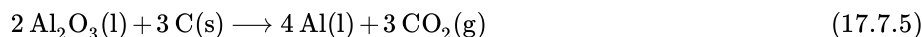


Figure 17.7.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and CaCl₂ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al₂O₃; melting point = 2054°C) and 95% cryolite (Na₃AlF₆; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO₂ gas at the carbon anode. The overall reaction is as follows:



Oxide ions react with oxidized carbon at the anode, producing CO₂(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and CaCl₂ is electrolyzed, Cl⁻ is oxidized because it is the only anion present, but either Na⁺ or Ca²⁺ can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al³⁺), but there are three species that can be oxidized: C, O²⁻, and F⁻.

In the Hall–Heroult process, C is oxidized instead of O²⁻ or F⁻ because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O₂ or F₂. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/CaCl₂ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca ($\chi = 0.93$ versus 1.00, respectively), making Na easier to oxidize and, conversely, Na⁺ more difficult to reduce. In fact, the reduction of Na⁺ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

✓ Example 17.7.1

If a molten mixture of MgCl₂ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

- List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
- Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2 . Because Mg is more electronegative than K ($\chi = 1.31$ versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2 .

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 17.7.1

Predict the products if a molten mixture of AlBr_3 and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2 . However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 17.7.3).

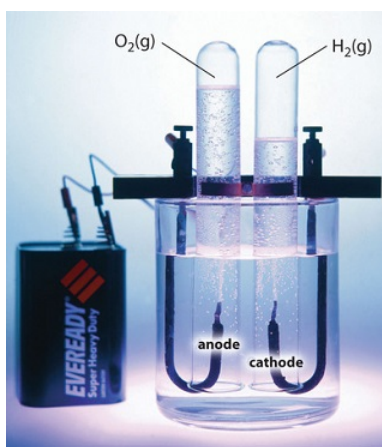


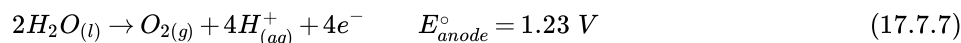
Figure 17.7.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

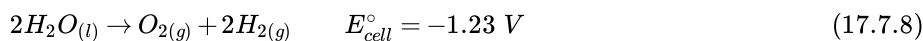
- cathode:



- anode:



- overall:



For a system that contains an electrolyte such as Na_2SO_4 , which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[\text{H}^{+}] = [\text{OH}^{-}] = 1.0 \times 10^{-7}$. Assuming that $P_{\text{O}_2} = P_{\text{H}_2} = 1\text{ atm}$, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{0.0591 \text{ V}}{n} \right) \log(P_{\text{O}_2} P_{\text{H}_2}^2) \quad (17.7.9)$$

$$= -1.23 \text{ V} - \left(\frac{0.0591 \text{ V}}{4} \right) \log(1) = -1.23 \text{ V} \quad (17.7.10)$$

Thus E_{cell} is -1.23 V , which is the value of E_{cell}° if the reaction is carried out in the presence of 1 M H^+ rather than at $\text{pH } 7.0$.

In practice, a voltage about $0.4\text{--}0.6 \text{ V}$ greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^- , SO_4^{2-} , PO_4^{3-} , are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 17.7.4.

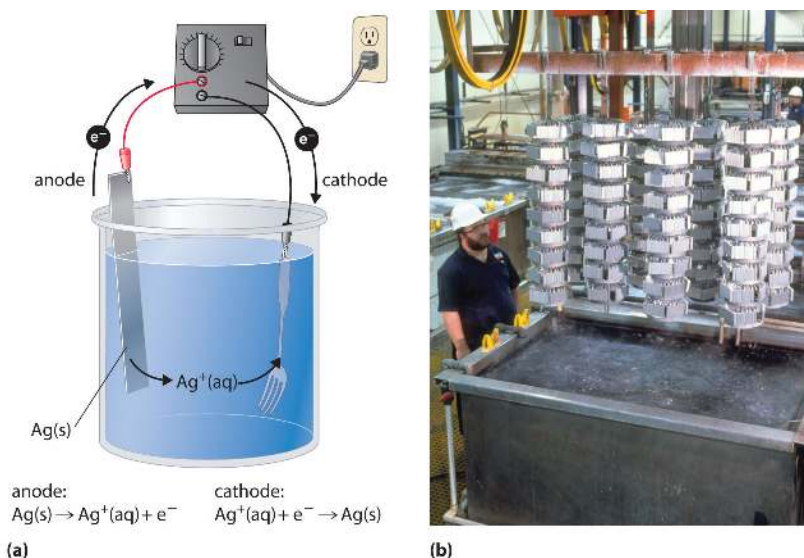
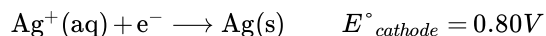


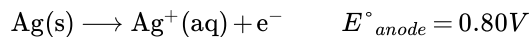
Figure 17.7.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):



- anode (silver bar):

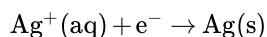


The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^\circ_{\text{cell}} = 0\text{ V}$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

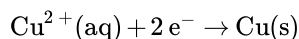
Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction



1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction



1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t , in seconds):

$$q = I \times t \quad (17.7.11)$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of CuSO_4 for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\text{ A})(6.0\text{ min})(60\text{ s/min}) \\ &= 220\text{ A} \cdot \text{s} \\ &= 220\text{ C} \end{aligned}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\text{ C}}{96,485\text{ C/mol}} \\ &= 2.3 \times 10^{-3}\text{ mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or $1.2 \times 10^{-3}\text{ mol}$. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

✓ Example 17.7.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

- Calculate the number of moles of metal corresponding to the given mass transferred.
- Write the reaction and determine the number of moles of electrons required for the electroplating process.
- Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00 \text{ g}}{107.868 \text{ g/mol}} = 1.85 \times 10^{-2} \text{ mol Ag}$$

B The reduction reaction is $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2} \text{ mol e}^-)(96,485 \text{ C/mol e}^-) = 1.78 \times 10^3 \text{ C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned} \text{amperes} &= \frac{1.78 \times 10^3 \text{ C}}{(12.0 \text{ h})(60 \text{ min/h})(60 \text{ s/min})} \\ &= 4.12 \times 10^{-2} \text{ C/s} = 4.12 \times 10^{-2} \text{ A} \end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

? Exercise 17.7.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten $\text{Al}_2\text{O}_3/\text{Na}_3\text{AlF}_6$ mixture?

Answer

5.8 h



Electroplating: [Electroplating\(opens in new window\)](#) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H₂ and O₂ from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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SECTION OVERVIEW

UNIT III: CHEMICAL BONDING AND STRUCTURE

UC Davis CHE 2CH Honors General Chemistry III

Unit I: Chemistry Fundamentals • Unit II: Bonding
Agenda • Homework Exercises • Worksheets

It is a "no brainer" to say that molecules are constructed of elements from the periodic table. These molecules can be separated into either organic or inorganic depending of which elements are used. The term organic is used to reference molecules that are primarily based on carbon, while the rest of the molecules are "inorganic." Although useful for study and research, this separation is not black/white as are most "rules" in chemistry.

7: Bonding in Organic Molecules

- 7.1: Petroleum Refining and the Hydrocarbons
- 7.2: The Alkanes
- 7.3: The Alkenes and Alkynes
- 7.4: Aromatic Hydrocarbons
- 7.5: Fullerenes
- 7.6: Functional Groups and Organic Reactions
- 7.7: Pesticides and Pharmaceuticals

8: Bonding in Transition Metal Compounds and Coordination Complexes

- 8.1: Chemistry of the Transition Metals
- 8.2: Bonding in Simple Molecules That Contain Transition Metals
- 8.3: Introduction to Coordination Chemistry
- 8.4: Structures of Coordination Complexes
- 8.5: Crystal Field Theory: Optical and Magnetic Properties
- 8.6: Optical Properties and the Spectrochemical Series
- 8.7: Bonding in Coordination Complexes

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CHAPTER OVERVIEW

7: Bonding in Organic Molecules

UC Davis CHE 2CH Honors General Chemistry III

Unit I: Chemistry Fundamentals • Unit II: Bonding
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[7.1: Petroleum Refining and the Hydrocarbons](#)

[7.2: The Alkanes](#)

[7.3: The Alkenes and Alkynes](#)

[7.4: Aromatic Hydrocarbons](#)

[7.5: Fullerenes](#)

[7.6: Functional Groups and Organic Reactions](#)

[7.7: Pesticides and Pharmaceuticals](#)

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7.1: Petroleum Refining and the Hydrocarbons

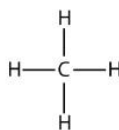
Learning Objectives

- To get an overview of hydrocarbons molecules and their four primary classifications

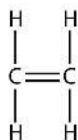
Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species. They are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is C_nH_{2n+2} (assuming non-cyclic structures). Saturated hydrocarbons are the basis of petroleum fuels and are found as either linear or branched species. The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:



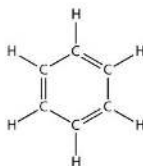
2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes and those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures). Those containing triple bonds are called alkynes, with general formula C_nH_{2n-2} . The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:



The smallest alkyne is ethyne, which is also known as acetylene:



3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n} .
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring. Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or "straight-run" alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes and alkynes due to the "self-bonding" or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

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7.2: The Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) and they are shown again in Figure 7.2.1.

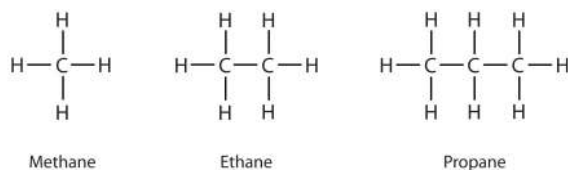


Figure 7.2.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 7.2.2).

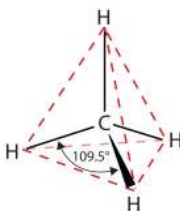


Figure 7.2.2: The Tetrahedral Methane Molecule

Methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH₂ unit. The first 10 members of this series are given in Table 7.2.1.

Table 7.2.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C _n H _{2n + 2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH ₄	CH ₄	—
ethane	C ₂ H ₆	CH ₃ CH ₃	—
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	—
butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2
pentane	C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	3

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 7.2.3. The sequence starts with C_3H_8 , and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

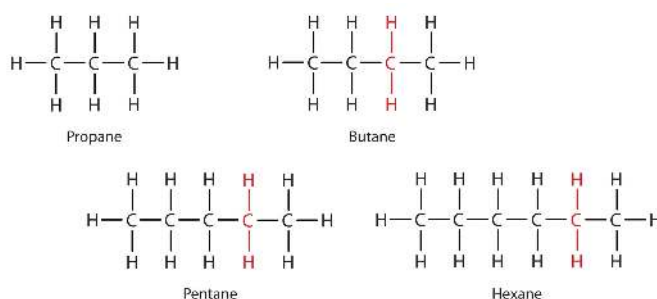


Figure 7.2.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2} . Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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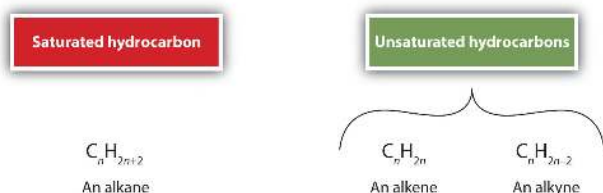
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7.3: The Alkenes and Alkynes

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R-C\equiv C-R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

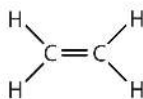


Some representative alkenes—their names, structures, and physical properties—are given in Table 7.3.1.

Table 7.3.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2=CH_2$	-169	-104
propene	C_3H_6	$CH_2=CHCH_3$	-185	-47
1-butene	C_4H_8	$CH_2=CHCH_2CH_3$	-185	-6
1-pentene	C_5H_{10}	$CH_2=CH(CH_2)_2CH_3$	-138	30
1-hexene	C_6H_{12}	$CH_2=CH(CH_2)_3CH_3$	-140	63
1-heptene	C_7H_{14}	$CH_2=CH(CH_2)_4CH_3$	-119	94
1-octene	C_8H_{16}	$CH_2=CH(CH_2)_5CH_3$	-102	121

We used only condensed structural formulas in Table 7.3.1. Thus, $CH_2=CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4 , whereas that for ethane is C_2H_6 .

The first two alkenes in Table 7.3.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 7.3.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

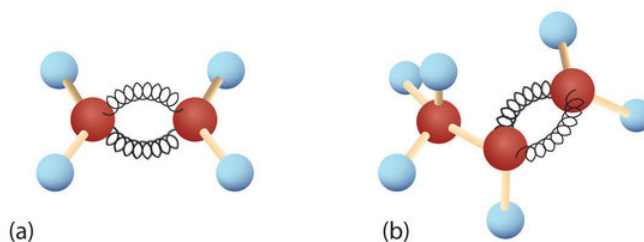
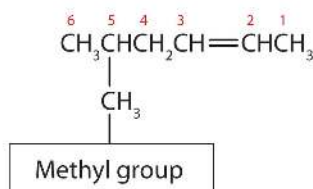


Figure 7.3.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8 .

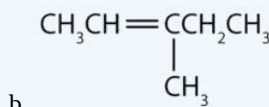
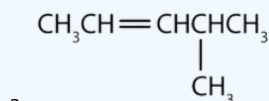
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2=CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers. The compound $CH_3CH=CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



✓ Example 7.3.1

Name each compound.

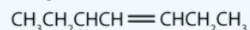
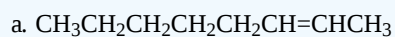


Solution

- a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
- b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

? Exercise 7.3.1

Name each compound.

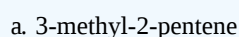


Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

✓ Example 7.3.2

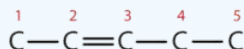
Draw the structure for each compound.



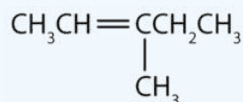
Solution

a.

First write the parent chain of five carbon atoms: $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$. Then add the double bond between the second and third carbon atoms:

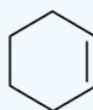


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



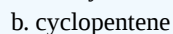
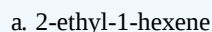
b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



? Exercise 7.3.2

Draw the structure for each compound.



Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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7.4: Aromatic Hydrocarbons

Learning Objectives

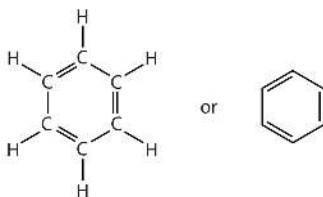
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14} —eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at $80^\circ C$, and freezes at $5.5^\circ C$. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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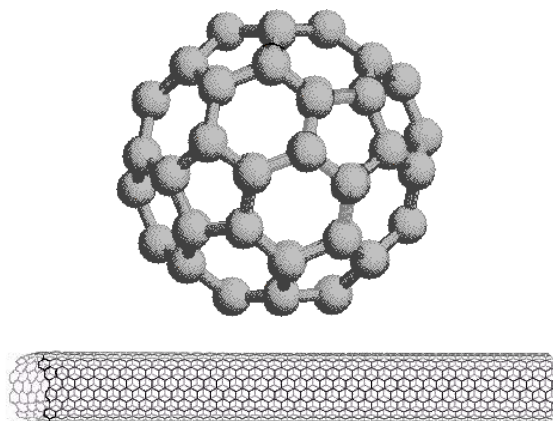
7.5: Fullerenes

If we extend the structure of corannulene by adding similar cycles of five benzene rings, the curvature of the resulting molecule should increase, and eventually close into a sphere of carbon atoms. The archetypical compound of this kind (C_{60}) has been named **buckminsterfullerene** because of its resemblance to the geodesic structures created by Buckminster Fuller. It is a member of a family of similar carbon structures that are called **fullerenes**. These materials represent a third class of carbon allotropes. Alternating views of the C_{60} fullerene structure are shown on the right, together with a soccer ball-like representation of the 12 five and 20 six-membered rings composing its surface. Precise measurement by Atomic Force Microscopy (AFM) has shown that the C-C bond lengths of the six-membered rings are not all equal, and depend on whether the ring is fused to a five or six-membered neighbor. [By clicking on this graphic, a model of \$C_{60}\$ will be displayed.](#)

Although C_{60} is composed of fused benzene rings its chemical reactivity resembles that of the cycloalkenes more than benzene. Indeed, exposure to light and oxygen slowly degrade fullerenes to cage opened products. Most of the reactions thus far reported for C_{60} involve addition to, rather than substitution of, the core structure. These reactions include hydrogenation, bromination and hydroxylation. Strain introduced by the curvature of the surface may be responsible for the enhanced reactivity of C_{60} .

Larger fullerenes, such as C_{70} , C_{76} , C_{82} & C_{84} have ellipsoidal or distorted spherical structures, and fullerene-like assemblies up to C_{240} have been detected. A fascinating aspect of these structures is that the space within the carbon cage may hold atoms, ions or small molecules. Such species are called **endohedral fullerenes**. The cavity of C_{60} is relatively small, but encapsulated helium, lithium and atomic nitrogen compounds have been observed. Larger fullerenes are found to encapsulate lanthanide metal atoms.

Interest in the fullerenes has led to the discovery of a related group of carbon structures referred to as nanotubes. As shown in the following illustration, nanotubes may be viewed as rolled up segments of graphite. The chief structural components are six-membered rings, but changes in tube diameter, branching into side tubes and the capping of tube ends is accomplished by fusion with five and seven-membered rings.



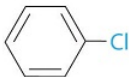
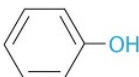
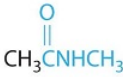
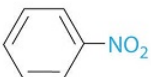
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7.6: Functional Groups and Organic Reactions

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 7.6.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

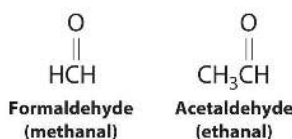
Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C=CR''R'''$	$H_2C=CH_2$	ethylene (ethene)	-ene
Alkynes	$RC\equiv CR'$	$HC\equiv CH$	acetylene (ethyne)	(-yne)
Arenes	ArH^a		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX^a		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH^a	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	$ArOH^b$		phenol	-ol
Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	$RCHO$		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C=O$		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	$RCONHR'$		N-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	$RNH_2, RNHR', RNR'R''$	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC\equiv N$	$H_3C\equiv N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2^a$		nitrobenzene	nitro-

^aR indicates an alkyl group ^bAr indicates an aryl group.

Figure 7.6.1: Major Classes of Organic Compounds

The first family listed in Figure 7.6.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n} ; alkynes, represented by C_nH_{2n-2} ; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $-CO_2H$ functional group is replaced by either an alkoxy ($-OR$) group, producing an ester, or by an amido ($-NRR'$, where R and R' can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a $C\equiv N$ bond; and nitro compounds, which contain the $-NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 7.6.2). In common nomenclature, in contrast, the prefixes *ortho*-, *meta*-, and *para*- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called *ortho*-xylene, abbreviated *o*-xylene. If they are across from each other on the ring, the compound is commonly called *para*-xylene or *p*-xylene. When the arrangement is intermediate between those of *ortho*- and *para*- compounds, the name is *meta*-xylene or *m*-xylene.

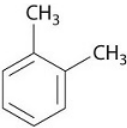
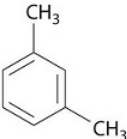
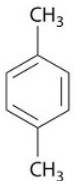
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
<i>ortho</i> -	1,2		<i>o</i> -xylene (1,2-dimethylbenzene)
<i>meta</i> -	1,3		<i>m</i> -xylene (1,3-dimethylbenzene)
<i>para</i> -	1,4		<i>p</i> -xylene (1,4-dimethylbenzene)

Figure 7.6.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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7.7: Pesticides and Pharmaceuticals

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CHAPTER OVERVIEW

8: Bonding in Transition Metal Compounds and Coordination Complexes

- 8.1: Chemistry of the Transition Metals
- 8.2: Bonding in Simple Molecules That Contain Transition Metals
- 8.3: Introduction to Coordination Chemistry
- 8.4: Structures of Coordination Complexes
- 8.5: Crystal Field Theory: Optical and Magnetic Properties
- 8.6: Optical Properties and the Spectrochemical Series
- 8.7: Bonding in Coordination Complexes

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8.1: Chemistry of the Transition Metals

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

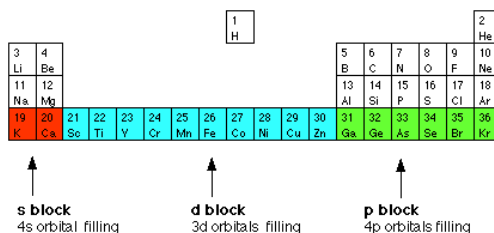
What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

d-block elements

You will remember that when you are building the [Periodic Table](#) and working out where to put the electrons using the [Aufbau Principle](#), something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



The electronic structures of the d block elements shown are:

Sc	[Ar] 3d ¹ 4s ²
Ti	[Ar] 3d ² 4s ²
V	[Ar] 3d ³ 4s ²
Cr	[Ar] 3d ⁵ 4s ¹
Mn	[Ar] 3d ⁵ 4s ²
Fe	[Ar] 3d ⁶ 4s ²
Co	[Ar] 3d ⁷ 4s ²
Ni	[Ar] 3d ⁸ 4s ²
Cu	[Ar] 3d ¹⁰ 4s ¹
Zn	[Ar] 3d ¹⁰ 4s ²

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

Transition metals

Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:

The official IUPAC definition:

A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.

The older definition:

A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure $[\text{Ar}] 3d^1 4s^2$. When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The Sc^{3+} ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure $[\text{Ar}] 3d^{10} 4s^2$. When it forms ions, it always loses the two 4s electrons to give a $2+$ ion with the electronic structure $[\text{Ar}] 3d^{10}$. The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper, $[\text{Ar}] 3d^{10} 4s^1$, forms two ions. In the Cu^+ ion the electronic structure is $[\text{Ar}] 3d^{10}$. However, the more common Cu^{2+} ion has the structure $[\text{Ar}] 3d^9$. Copper is definitely a transition metal because the Cu^{2+} ion has an incomplete d level.

Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the [Aufbau Principle](#), you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for Co^{2+} :

Co		$[\text{Ar}] 3d^7 4s^2$
Co^{2+}		$[\text{Ar}] 3d^7$

The $2+$ ion is formed by the loss of the two 4s electrons.

To write the electronic structure for V^{3+} :

V		$[\text{Ar}] 3d^3 4s^2$
V^{3+}		$[\text{Ar}] 3d^2$

The 4s electrons are lost first followed by one of the 3d electrons.

Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of [oxidation states](#) (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

Examples of variable oxidation states in the transition metals

- Iron:** Iron has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+} . It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-} .
- Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

+2	in Mn^{2+}
----	---------------------

+3	in Mn_2O_3
+4	in MnO_2
+6	in MnO_4^{2-}
+7	in MnO_4^-

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+} . When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is CaCl_2 . Why is that? If you tried to make CaCl , (containing a Ca^+ ion), the overall process is slightly exothermic. By making a Ca^{2+} ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a $1+$ ion. The overall process is very exothermic. Because the formation of CaCl_2 releases much more energy than making CaCl , then CaCl_2 is more stable - and so forms instead.

What about CaCl_3 ? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make CaCl_3 !

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the $2+$ or the $3+$ ion.

Fe		$[\text{Ar}] 3d^6 4s^2$
Fe^{2+}		$[\text{Ar}] 3d^6$
Fe^{3+}		$[\text{Ar}] 3d^5$

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in kJ mol^{-1}) for iron compared with those of calcium are:

metal	1st IE	2nd IE	3rd IE
Ca	590	1150	4940
Fe	762	1560	2960

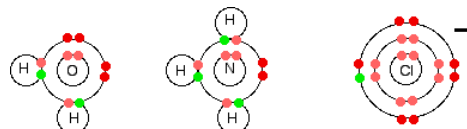
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, FeCl_2 or FeCl_3 . That means that it is not too difficult to convert between the two compounds.

The formation of complex ions

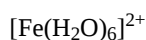
What is a complex ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

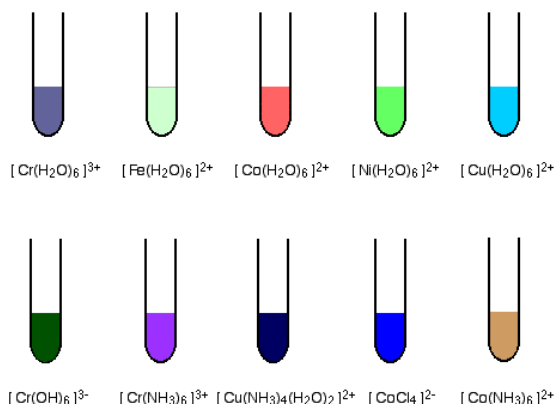
Some examples of complex ions formed by transition metals



Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals.

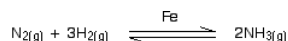
Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The [Haber Process](#) combines hydrogen and nitrogen to make ammonia using an iron catalyst.



Nickel in the hydrogenation of C=C bonds

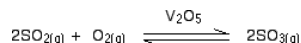
This reaction is at the heart of the manufacture of [margarine](#) from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



Transition metal compounds as catalysts

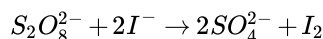
Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.



Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $\text{S}_2\text{O}_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.



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8.2: Bonding in Simple Molecules That Contain Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the [transition metals](#) have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on [atomic orbitals](#).

Table 8.2.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x , p_y , p_z ; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{yz} , d_{xz} ; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number $n+1$

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the [Periodic Table](#).

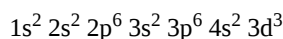
1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on [electron configuration](#).

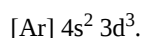
Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.



OR



The neutral atom configurations of the fourth period transition metals are in Table 8.2.2.

Table 8.2.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] 4s ² 3d ¹	[Ar] 4s ² 3d ²	[Ar] 4s ² 3d ³	[Ar] 4s ² 3d ⁴	[Ar] 4s ² 3d ⁵	[Ar] 4s ² 3d ⁶	[Ar] 4s ² 3d ⁷	[Ar] 4s ² 3d ⁸	[Ar] 4s ² 3d ⁹	[Ar] 4s ² 3d ¹⁰
			[Ar] 4s ¹ 3d ⁵					[Ar] 4s ¹ 3d ¹⁰	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 8.2.1). The electronic configuration for chromium is not [Ar] 4s²3d⁴ but instead it is [Ar] 4s¹3d⁵. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 8.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose its s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see [formation of coordination complexes](#).

✓ Example 8.2.1

Write the electronic configurations of:

- neutral iron,
- iron(II) ion, and
- iron(III) ion.

Answer

The atomic number of iron is 26 so there are 26 protons in the species.

- Fe: $[\text{Ar}] 4s^2 3d^6$
- Fe^{2+} : $[\text{Ar}] 3d^6$
- Fe^{3+} : $[\text{Ar}] 3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

✓ Example 8.2.2

Determine the more stable configuration between the following pair:

- $[\text{Kr}] 5s^2 4d^6$ vs. $[\text{Kr}] 5s^1 4d^7$
- Ag^{1+} vs. Ag^{2+}

Answer

- This describes Ruthenium. There is only one 5s electron.
- Once-oxidized silver ($[\text{Kr}] 4d^{10}$) is more stable than twice- ($[\text{Kr}] 4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] 4s ² 3d ¹	Sc: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$
Titanium (Ti)	22	+4	Ti: [Ar] 4s ² 3d ²	Ti: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] 4s ² 3d ³	V: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] 4s ¹ 3d ⁵	Cr: [Ar] $\frac{1}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] 4s ² 3d ⁵	Mn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Iron (Fe)	26	+2, +3	Fe: [Ar] 4s ² 3d ⁶	Fe: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Cobalt (Co)	27	+2, +3	Co: [Ar] 4s ² 3d ⁷	Co: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Nickel (Ni)	28	+2	Ni: [Ar] 4s ² 3d ⁸	Ni: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1}{3d}$ $\frac{1}{3d}$
Copper (Cu)	29	+1, +2	Cu: [Ar] 4s ¹ 3d ¹⁰	Cu: [Ar] $\frac{1}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Zinc (Zn)	30	+2	Zn: [Ar] 4s ² 3d ¹⁰	Zn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

✓ Example 8.2.3

What makes zinc stable as Zn²⁺? What makes scandium stable as Sc³⁺?

Answer

Zinc has the neutral configuration [Ar]4s²3d¹⁰. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as [Ar]4s²3d¹. Losing 3 electrons brings the configuration to the noble state with valence 3p⁶.

✓ Example 8.2.4

Why is iron almost always Fe²⁺ or Fe³⁺?

Answer

Iron is written as [Ar]4s²3d⁶. Losing 2 electrons from the s-orbital (3d⁶) or 2 s- and 1 d-orbital (3d⁵) electron are fairly stable oxidation states.

✓ Example 8.2.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

Answer

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $\text{Mn}_{(s)}$, Mn(II) as MnO , Mn(II,III) as Mn_3O_4 , Mn(IV) as MnO_2 , or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^- , and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as AgCl , you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the **halogen** group of the periodic table, we then know that it has a charge of -1, or simply Cl^- . In addition, by seeing that there is no overall charge for AgCl , (which is determined by looking at the top right of the compound, i.e., $\text{AgCl}^\#$, where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag^+ and Cl^- , in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

✓ Example 8.2.6

Determine the oxidation state of cobalt in CoBr_2 .

Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 (Br^-). Since there are two bromines each with a charge of -1. In addition, we know that CoBr_2 has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

✓ Example 8.2.7

What is the oxidation state of zinc in ZnCO_3 . (Note: the CO_3 anion has a charge state of -2)

Answer

Knowing that CO_3 has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us Zn^{2+} and CO_3^{2-} , in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (MnO_4^-) ion. Since **oxygen** has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us Mn^{7+} and 4O^{2-} , which will result as MnO_4^- .

This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.

📌 Manganese: A Case Study

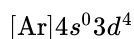
Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.



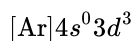
Figure 8.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

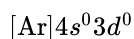
Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.



MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+} .



KMnO_4 is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.



Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the [formation of coordination complexes](#) or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) <u>Copper</u> (I) Chloride: CuCl	(B) <u>Copper</u> (II) Nitrate: $\text{Cu}(\text{NO}_3)_2$	(C) <u>Gold</u> (V) Fluoride: AuF_5
(D) <u>Iron</u> (II) Oxide: FeO	(E) <u>Iron</u> (III) Oxide: Fe_2O_3	(F) <u>Lead</u> (II) Chloride: PbCl_2
(G) <u>Lead</u> (II) Nitrate: $\text{Pb}(\text{NO}_3)_2$	(H) <u>Manganese</u> (II) Chloride: MnCl_2	(I) <u>Molybdenum</u> trioxide: MoO_3
(J) <u>Nickel</u> (II) Hydroxide: $\text{Ni}(\text{OH})_2$	(K) <u>Platinum</u> (IV) Chloride: PtCl_4	(L) <u>Silver</u> Sulfide: Ag_2S
(M) <u>Tungsten</u> (VI) Fluoride: WF_6	(N) <u>Vanadium</u> (III) Nitride: VN	(O) <u>Zirconium</u> Hydroxide: $\text{Zr}(\text{OH})_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate (MnO_4^{2-})
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

References

1. Oxtoby D, Gillis H P, Campion, A. *Principles of Modern Chemistry*, 6th ed. Thomson Brooks/Cole, Belmont. 2008; 313-318.
2. Audi A, Sherwood, P. *Valence-band x-ray photoelectron spectroscopic studies of manganese and its oxides interpreted by cluster and band structure calculations*; Surf. Interface Anal.; 2002; 33; 274-282.
3. Reaney S, Kwik-Urbe C, Smith D. *Manganese Oxidation State and Its Implications for Toxicity*. Chem. Res. Toxicol.; 2002; 15; 1119-1126.
4. *CRC Handbook*, 88th ed. Sct. 1, Prt. 1 *Electron Configuration and Ionization Energy of Neutral Atoms in the Ground State*; 13-14.
5. *CRC Handbook*, 88th ed. Sct. 4, Prt. 1 *Melting, Boiling, Triple, and Critical Point Temperatures of the Elements*; 133-134.

Contributors and Attributions

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8.3: Introduction to Coordination Chemistry

Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by **coordinate (dative covalent) bonds** (in some cases, the bonding is actually more complicated than that). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

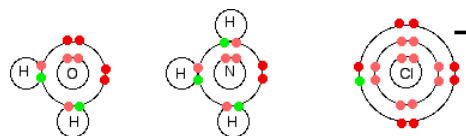


Figure 8.3.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

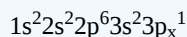
What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as **Lewis bases**.

Bonding in Simple Complex Ions

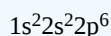
We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

✓ Example 8.3.1: $\text{Al}(\text{H}_2\text{O})_6^{3+}$

Aluminum has the electronic structure

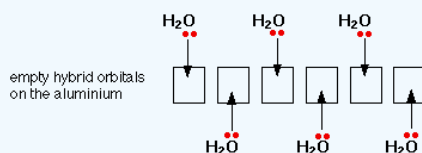


When it forms an Al^{3+} ion it loses the 3-level electrons to leave

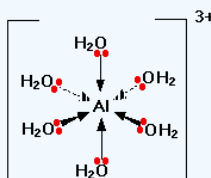


That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



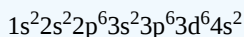
Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of

the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

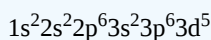
In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

✓ Example 8.3.2: $Fe(H_2O)_6^{3+}$

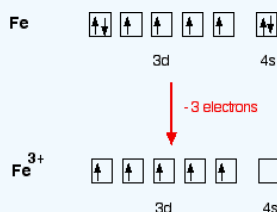
Iron has the electronic structure



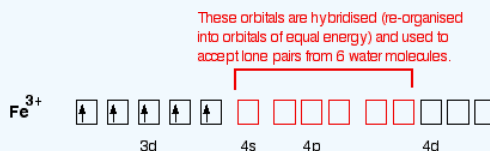
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave



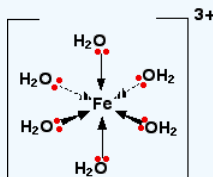
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.

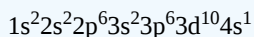


Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

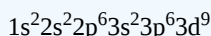
✓ Example 8.3.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

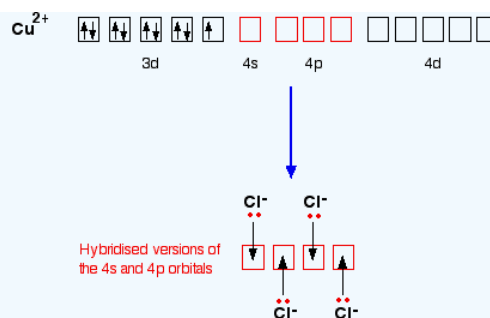
Copper has the electronic structure



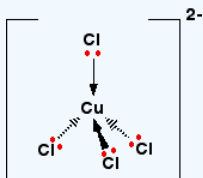
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave



To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Contributors and Attributions

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8.4: Structures of Coordination Complexes

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(\text{NH}_3)_2\text{PtCl}_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

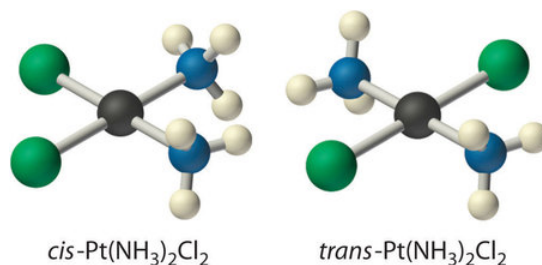


Figure 8.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of [coordination compounds](#) bond together is discussed in the chapter of [Lewis acids and bases](#). For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by [MIT](#) chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two amines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

? Exercise 8.4.1

Draw the cis and trans isomers of the following compounds:

- $(\text{NH}_3)_2\text{IrCl}(\text{CO})$
- $(\text{H}_3\text{P})_2\text{PtHBr}$
- $(\text{AsH}_3)_2\text{PtH}(\text{CO})$

? Exercise 8.4.2

Only one isomer of $(\text{tmeda})\text{PtCl}_2$ is possible [$\text{tmeda} = (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

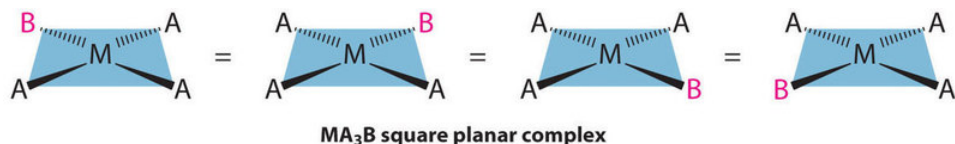
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called **geometrical isomers**. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (**cis**), in which case the B ligands must also be cis, or the A ligands can be across from one another (**trans**), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

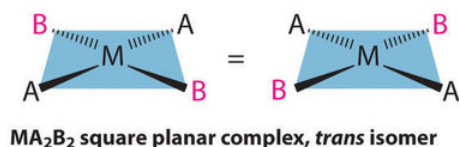
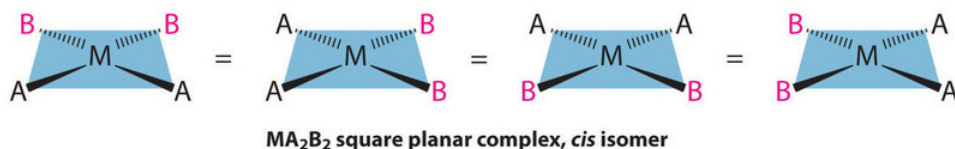
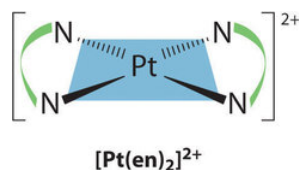


Figure 8.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed

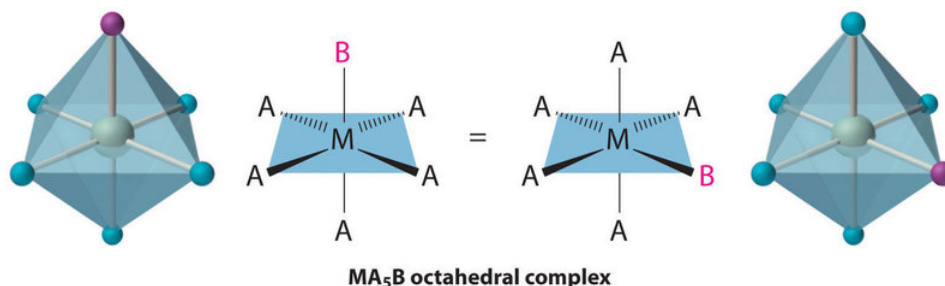
with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

Square planar complexes that contain symmetrical bidentate ligands, such as $[\text{Pt}(\text{en})_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:

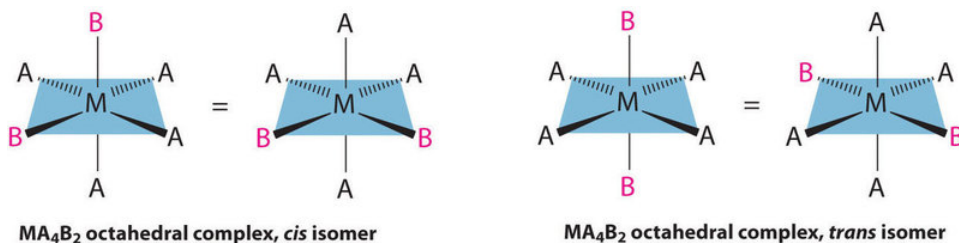


Octahedral Isomers

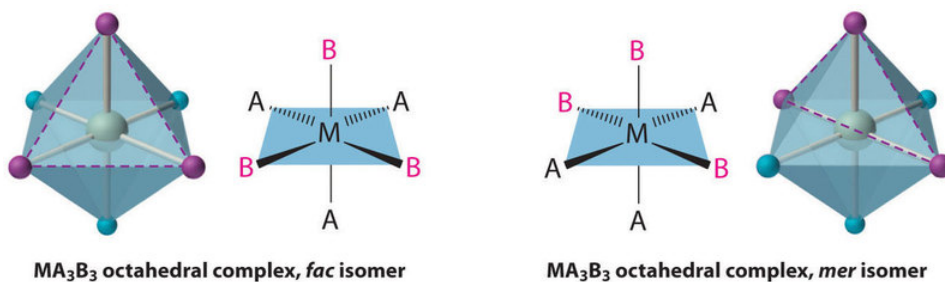
Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ are examples of this type of system:



Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



✓ Example 8.4.1

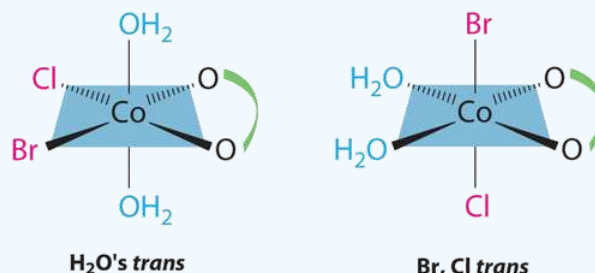
Draw all the possible geometrical isomers for the complex $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})\text{BrCl}]^-$, where ox is $^-\text{O}_2\text{CCO}_2^-$, which stands for oxalate.

Given: formula of complex

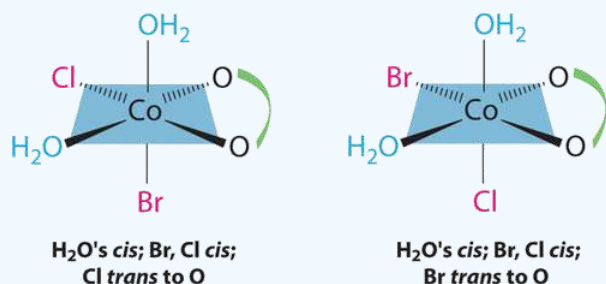
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



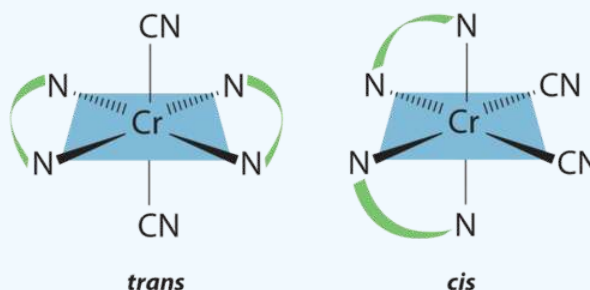
This complex can therefore exist as four different geometrical isomers.

? Exercise 8.4.1

Draw all the possible geometrical isomers for the complex $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

Contributors and Attributions

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8.5: Crystal Field Theory: Optical and Magnetic Properties

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five $(n - 1)d$ orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure 8.5.1a). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure 8.5.1b the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy} , d_{xz} , and d_{yz} , collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

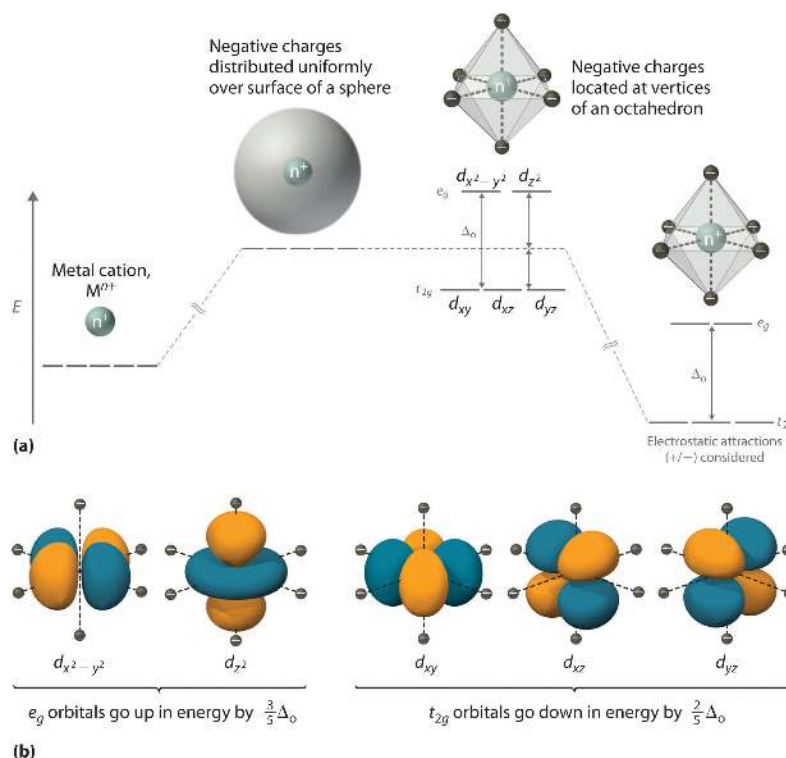


Figure 8.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of -6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of -1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the d_{xy} , d_{xz} , and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a -6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t .) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

Crystal field splitting does not change the total energy of the d orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 8.5.1a).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 8.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1 – d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins

parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

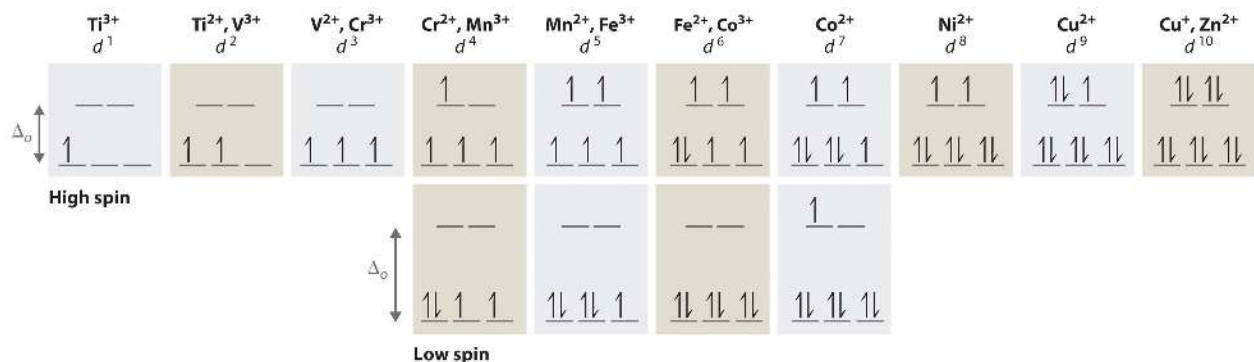


Figure 8.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes ($n = 1-10$). Two different configurations are possible for octahedral complexes of metals with d^4 , d^5 , d^6 , and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the **spin-pairing energy (P)**. If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[\text{Mn}(\text{CN})_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5 , d^6 , or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o .

In contrast, only one arrangement of d electrons is possible for metal ions with d^8 – d^{10} electron configurations. For example, the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ion is d^{10} with no unpaired electrons.

If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 8.5.1.

Table 8.5.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	20,300	$[\text{Fe}(\text{CN})_6]^{4-}$	32,800	VCl_4	9010
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12,600	$[\text{Fe}(\text{CN})_6]^{3-}$	35,000	$[\text{CoCl}_4]^{2-}$	3300
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	18,900	$[\text{CoF}_6]^{3-}$	13,000	$[\text{CoBr}_4]^{2-}$	2900
$[\text{CrCl}_6]^{3-}$	13,000	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9300	$[\text{CoI}_4]^{2-}$	2700

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: $1 \text{ cm}^{-1} = 11.96 \text{ J/mol}$.

Octahedral Complexes	Δ_o (cm ⁻¹)	Octahedral Complexes	Δ_o (cm ⁻¹)	Tetrahedral Complexes	Δ_t (cm ⁻¹)
[Cr(H ₂ O) ₆] ²⁺	13,900	[Co(H ₂ O) ₆] ³⁺	27,000		
[Cr(H ₂ O) ₆] ³⁺	17,400	[Co(NH ₃) ₆] ³⁺	22,900		
[Cr(NH ₃) ₆] ³⁺	21,500	[Co(CN) ₆] ³⁻	34,800		
[Cr(CN) ₆] ³⁻	26,600	[Ni(H ₂ O) ₆] ²⁺	8500		
Cr(CO) ₆	34,150	[Ni(NH ₃) ₆] ²⁺	10,800		
[MnCl ₆] ⁴⁻	7500	[RhCl ₆] ³⁻	20,400		
[Mn(H ₂ O) ₆] ²⁺	8500	[Rh(H ₂ O) ₆] ³⁺	27,000		
[MnCl ₆] ³⁻	20,000	[Rh(NH ₃) ₆] ³⁺	34,000		
[Mn(H ₂ O) ₆] ³⁺	21,000	[Rh(CN) ₆] ³⁻	45,500		
[Fe(H ₂ O) ₆] ²⁺	10,400	[IrCl ₆] ³⁻	25,000		
[Fe(H ₂ O) ₆] ³⁺	14,300	[Ir(NH ₃) ₆] ³⁺	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm⁻¹); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm⁻¹ = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for [V(H₂O)₆]²⁺, Δ_o = 11,800 cm⁻¹; for [V(H₂O)₆]³⁺, Δ_o = 17,850 cm⁻¹.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[\text{Co}(\text{NH}_3)_6]^{3+}: \Delta_o = 22,900 \text{ cm}^{-1}$$

$$[\text{Rh}(\text{NH}_3)_6]^{3+}: \Delta_o = 34,100 \text{ cm}^{-1}$$

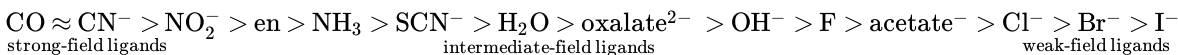
$$[\text{Ir}(\text{NH}_3)_6]^{3+}: \Delta_o = 40,000 \text{ cm}^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ because smaller, more localized charges, such as we see for F^- , interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3 , results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^- . The

experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o :



The values of Δ_o listed in Table 8.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o .

Figure 8.5.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o , which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o , which depends on the structure of the complex. For example, the complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o . Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[\text{Si}_6\text{O}_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o . Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 8.5.2 gives CFSE values for octahedral complexes with different d electron

configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 8.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δ_o)

	High Spin		CFSE (Δ_o)		Low Spin		CFSE (Δ_o)
d^0			0				
d^1	1		0.4				
d^2	1 1		0.8				
d^3	1 1 1		1.2				
d^4	1 1 1	1	0.6	1 ↓ 1 1			1.6
d^5	1 1 1	1 1	0.0	1 ↓ 1 ↓ 1			2.0
d^6	1 ↓ 1 1	1 1	0.4	1 ↓ 1 ↓ 1 ↓			2.4
d^7	1 ↓ 1 ↓ 1	1 1	0.8	1 ↓ 1 ↓ 1 ↓	1		1.8
d^8	1 ↓ 1 ↓ 1 ↓	1 1	1.2				
d^9	1 ↓ 1 ↓ 1 ↓	1 ↓ 1	0.6				
d^{10}	1 ↓ 1 ↓ 1 ↓	1 ↓ 1 ↓	0.0				

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

Octahedral d^3 and d^8 complexes and low-spin d^6 , d^5 , d^7 , and d^4 complexes exhibit large CFSEs.

✓ Example 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

- $[\text{CoF}_6]^{3-}$
- $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

- From the number of ligands, determine the coordination number of the compound.
- Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
- Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
- Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

- A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o , making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o , making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy} ; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$ orbital empty. Thus there are no unpaired electrons.

? Exercise 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

b. $[\text{PtCl}_4]^{2-}$

Answers

a. octahedral; high spin; five

b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o , whereas weak-field ligands interact more weakly and give a smaller Δ_o . The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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8.6: Optical Properties and the Spectrochemical Series

Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 8.6.1).

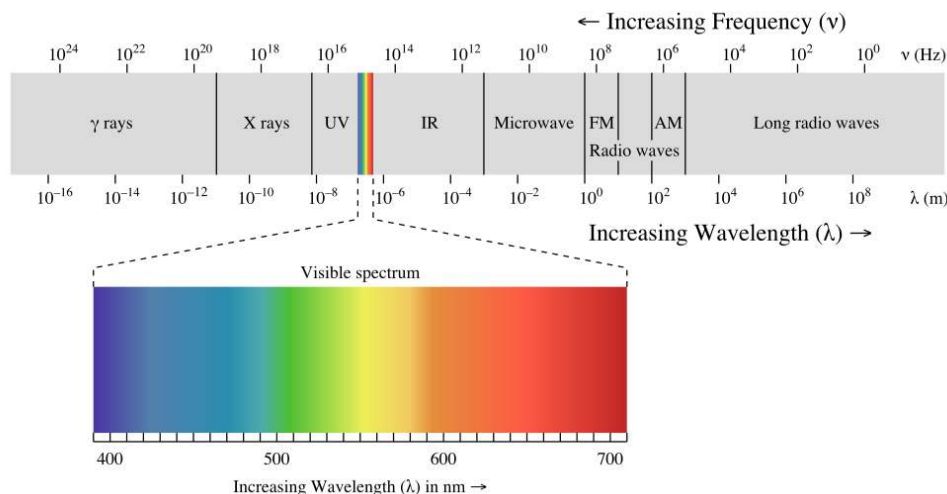


Figure 8.6.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light (c) is always a constant ($2.99792458 \times 10^8 \text{ m s}^{-1}$).
3. Wavelengths (λ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency (ν) of the photon

$$E = h\nu \quad (8.6.1)$$

since $\lambda\nu = c$ for all light Planck's law can be also expressed in terms of the wavelength of the photon

$$E = h\nu = \frac{hc}{\lambda} \quad (8.6.2)$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 8.6.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

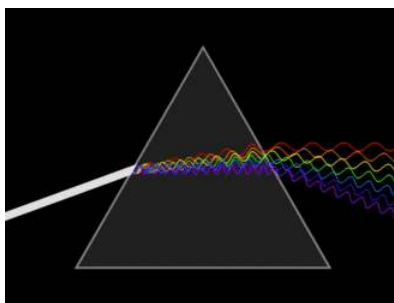
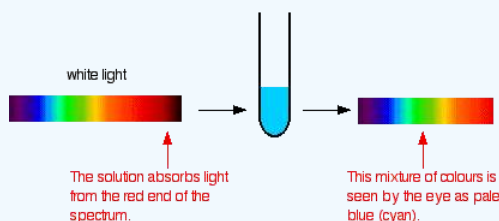


Figure 8.6.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

✓ Example 8.6.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Equation 8.6.4 is the most important equation in the field of light-matter interactions (spectroscopy).

As Example 8.6.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 8.6.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

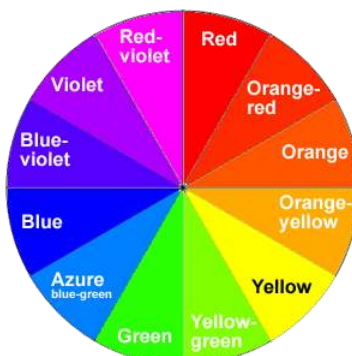


Figure 8.6.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 8.6.1).

Table 8.6.1: The Visible Spectrum

Color	Wavelength (nm)	ΔE HOMO - LUMO gap (eV)
UV	100 - 400	12.4 - 3.10
Violet	400 - 425	3.10 - 2.92
Blue	425 - 492	2.92 - 2.52
Green	492 - 575	2.52 - 2.15
Yellow	575 - 585	2.15 - 2.12
Orange	585 - 647	2.12 - 1.92
Red	647 - 700	1.92 - 1.77
Near IR	700 - 10,000	1.77 - 0.12

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light $\Rightarrow$ color is yellow
- the material absorbs blue light $\Rightarrow$ color is orange
- the material absorbs yellow-green light $\Rightarrow$ color is red-violet

The Origin of Color in Complex Ions

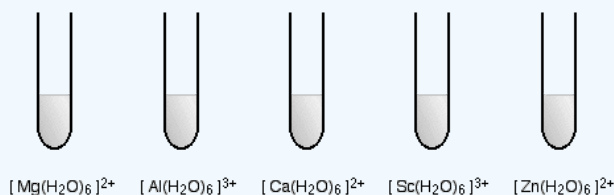
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called **d block elements** rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] 3d¹⁰4s² does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] 3d¹4s²) does not

really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

✓ Example 8.6.3: Hexaaqua Metal Ions

The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\text{M}(\text{H}_2\text{O})_6]^{n+}$. The charge on these ions is typically 2+ or 3+.

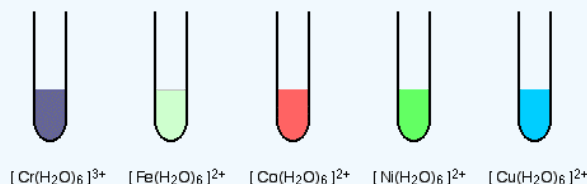
- Non-transition metal ions



These ions are all colorless.

Ions are $[\text{Mg}(\text{H}_2\text{O})_6]$ two plus, $[\text{Al}(\text{H}_2\text{O})_6]$ three plus, $[\text{Ca}(\text{H}_2\text{O})_6]$ two plus, $[\text{Sc}(\text{H}_2\text{O})_6]$ three plus, and $[\text{Zn}(\text{H}_2\text{O})_6]$ two plus

- Transition metal ions



Ions are $[\text{Cr}(\text{H}_2\text{O})_6]$ three plus, $[\text{Fe}(\text{H}_2\text{O})_6]$ two plus, $[\text{Co}(\text{H}_2\text{O})_6]$ two plus, $[\text{Ni}(\text{H}_2\text{O})_6]$ two plus, and $[\text{Cu}(\text{H}_2\text{O})_6]$ two plus.

The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

Magnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only the first two are introduced below.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. **Hund's Rule** states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.

As shown in the video, molecular oxygen (O_2) is paramagnetic and is attracted to the magnet. In contrast, Molecular nitrogen, N_2 , however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+} , Ti^{4+} , Zn^{2+} , and Cu^+ . These metals are not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the [Pauli Exclusion Principle](#) which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly **repelled** by a magnetic field. In fact, diamagnetic substances are weakly **repelled** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 8.6.6.

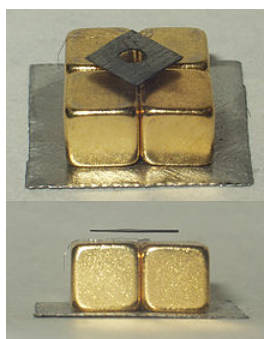


Figure 8.6.6: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

📌 How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration

2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more unpaired electrons) or diamagnetic (all electrons paired)

✓ Example 8.6.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

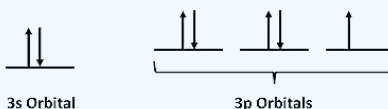
Solution

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^23p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

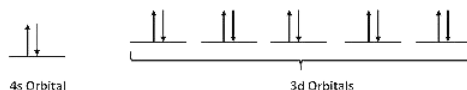
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^23d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

References

1. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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8.7: Bonding in Coordination Complexes

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth (**dent**) is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 8.7.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

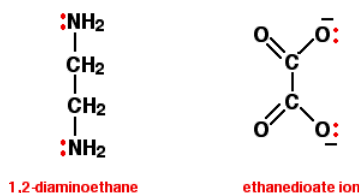
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek *chelos*, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

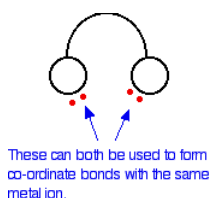
In the examples previously discussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

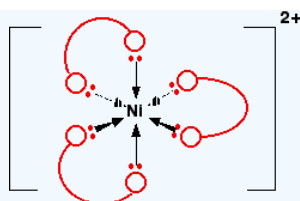


In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snugly around a metal ion.



✓ Example 8.7.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH_2 groups - and the "bit that goes over your head" is the $-\text{CH}_2\text{CH}_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

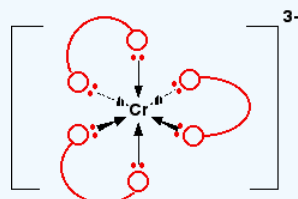
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

✓ Example 5: $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3.$$

The structure of the ion looks like this:

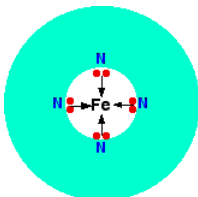


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

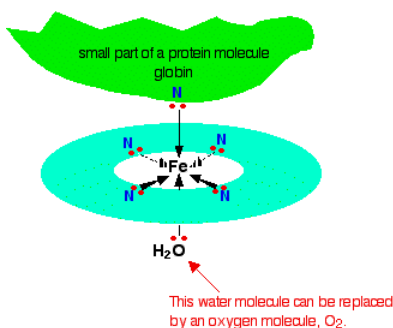


Figure 8.7.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

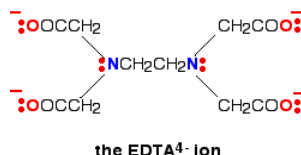
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O₂) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

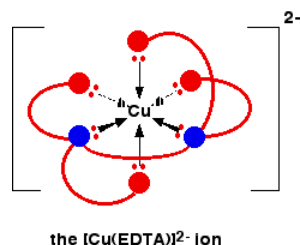
You probably know that carbon monoxide is poisonous because it reacts with haemoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that haemoglobin molecule useless for any further oxygen transfer.

A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the EDTA⁴⁻ ion.

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CHAPTER OVERVIEW

UNIT IV: MOLECULAR SPECTROSCOPY

Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules (or atomic or molecular ions) to qualitatively or quantitatively study the atoms or molecules, or to study physical processes. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule is called absorption. A transition from a higher level to a lower level is called emission if energy is transferred to the radiation field, or nonradiative decay if no radiation is emitted. Redirection of light due to its interaction with matter is called scattering, and may or may not occur with transfer of energy, i.e., the scattered radiation has a slightly different or the same wavelength.

[20.1: General Aspects of Molecular Spectroscopy](#)

[20.2: Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy](#)

[20.3: Excited Electronic States: Electronic Spectroscopy of Molecules](#)

[20.4: Nuclear Magnetic Resonance Spectroscopy](#)

[20.5: Introduction to Atmospheric Photochemistry](#)

[20.6: Photosynthesis](#)

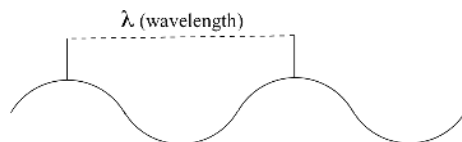
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20.1: General Aspects of Molecular Spectroscopy

The electromagnetic spectrum

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy*.



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as ‘wave-particle duality’: at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable ‘wavelength’). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = \frac{hc}{\lambda} \quad (4.1.1)$$

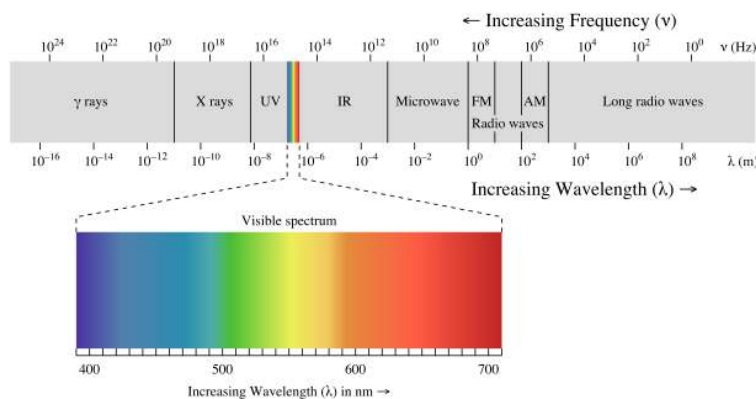
where E is energy in kJ/mol, λ (the Greek letter *lambda*) is wavelength in meters, c is 3.00×10^8 m/s (the speed of light), and h is 3.99×10^{-13} kJ·s·mol⁻¹, a number known as **Planck’s constant**.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning ‘cycles per second’, or ‘waves per second’. The standard unit for frequency is s⁻¹.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda\nu = c \quad (4.1.2)$$

where ν (the Greek letter ‘nu’) is frequency in s⁻¹. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29×10^{14} Hz, and an energy of 40.9 kcal per mole of photons. The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



(Image from [Wikipedia commons](#))

Notice that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

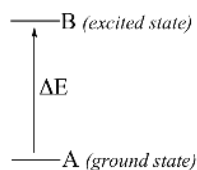
Exercise 4.4: Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kJ/mol of photons?

[Solutions](#)

Overview of a molecular spectroscopy experiment

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy 'ground state' to some higher energy 'excited state'. Other wavelengths are *not* absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.

Here is the key to molecular spectroscopy: *a given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring.* Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of ΔE , the molecule will specifically absorb radiation with wavelength that corresponds to ΔE , while allowing other wavelengths to pass through unabsorbed.



By observing which wavelengths a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.

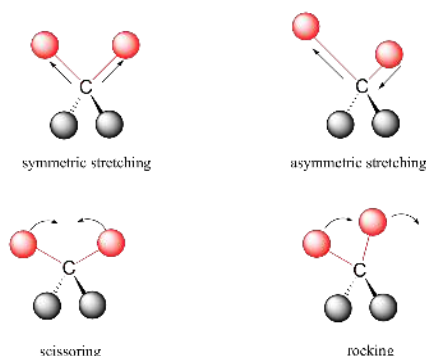
These generalized ideas may all sound quite confusing at this point, but things will become much clearer as we begin to discuss specific examples.

[Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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20.2: Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy

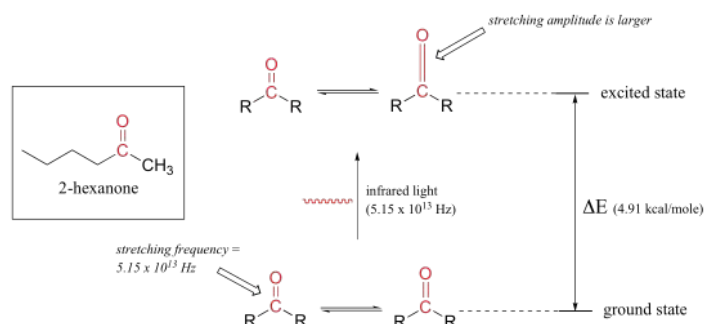
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.



The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

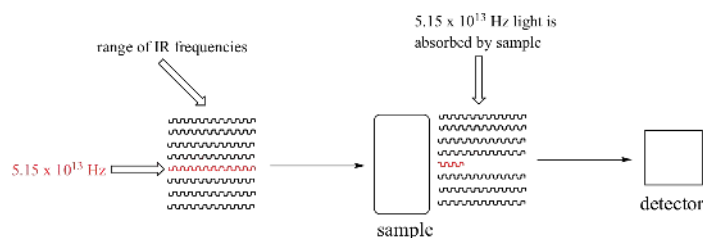
Let's take 2-hexanone as an example. Picture the carbonyl bond of the ketone group as a spring that is constantly bouncing back and forth, stretching and compressing, pushing the carbon and oxygen atoms further apart and then pulling them together. This is the **stretching mode** of the carbonyl bond. In the space of one second, the spring 'bounces' back and forth 5.15×10^{13} times - in other words, the ground-state frequency of carbonyl stretching for a the ketone group is about 5.15×10^{13} Hz.

If our ketone sample is irradiated with infrared light, the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83×10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of ΔE - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed through our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.



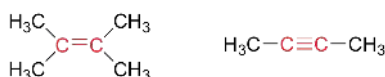
Our 5.15×10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of $5.11 - 5.18 \times 10^{13}$ Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range $6.30 - 6.80 \times 10^{13}$ Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

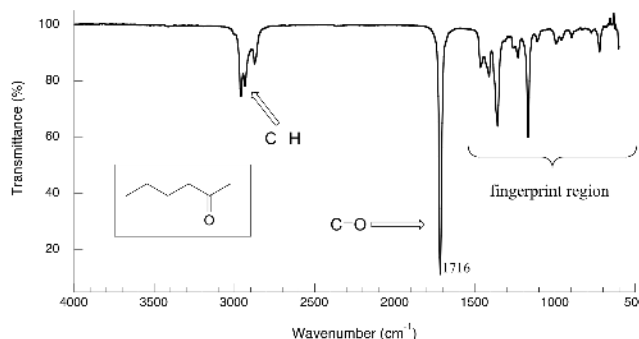
Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. *In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule.* Such vibrations are said to be **infrared active**. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.

Some kinds of vibrations are **infrared inactive**. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules *do* absorb IR light).



infrared-inactive double and triple bonds

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see '% transmittance', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of %

transmittance for every wavelength – the ‘peaks’ (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The ‘upside down’ vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn’t want to make things too easy for you!

Exercise 4.5: Express the wavenumber value of 3000 cm^{-1} in terms of wavelength (in meter units) frequency (in Hz), and associated energy (in kJ/mol).

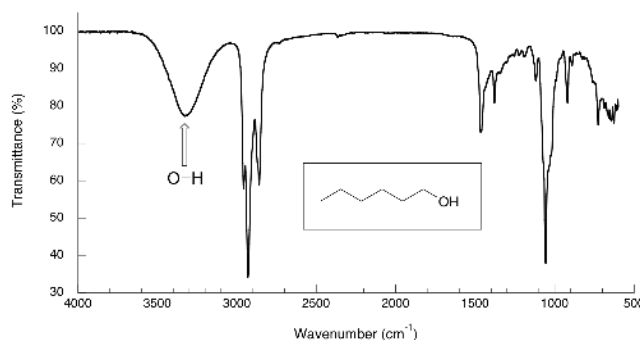
[Solutions](#)

The key absorption peak in this spectrum is that from the carbonyl double bond, at 1716 cm^{-1} (corresponding to a wavelength of 5.86 mm , a frequency of $5.15 \times 10^{13}\text{ Hz}$, and a ΔE value of 4.91 kcal/mol). Notice how strong this peak is, relative to the others on the spectrum: *a strong peak in the $1650\text{--}1750\text{ cm}^{-1}$ region is a dead giveaway for the presence of a carbonyl group*. Within that range, carboxylic acids, esters, ketones, and aldehydes tend to absorb in the shorter wavelength end ($1700\text{--}1750\text{ cm}^{-1}$), while conjugated unsaturated ketones and amides tend to absorb on the longer wavelength end ($1650\text{--}1700\text{ cm}^{-1}$).

The jagged peak at approximately $2900\text{--}3000\text{ cm}^{-1}$ is characteristic of tetrahedral carbon-hydrogen bonds. This peak is not terribly useful, as just about every organic molecule that you will have occasion to analyze has these bonds. Nevertheless, it can serve as a familiar reference point to orient yourself in a spectrum.

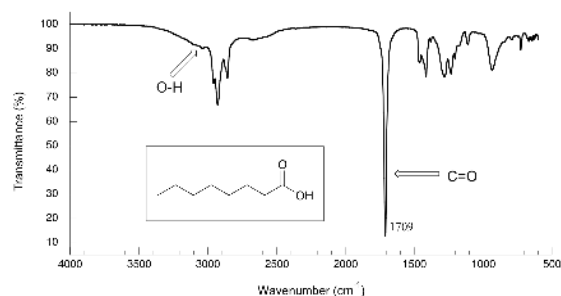
You will notice that there are many additional peaks in this spectrum in the longer-wavelength $400\text{--}1400\text{ cm}^{-1}$ region. This part of the spectrum is called the **fingerprint region**. While it is usually very difficult to pick out any specific functional group identifications from this region, it does, nevertheless, contain valuable information. The reason for this is suggested by the name: just like a human fingerprint, the pattern of absorbance peaks in the fingerprint region is unique to every molecule, meaning that the data from an unknown sample can be compared to the IR spectra of known standards in order to make a positive identification. It was the IR fingerprint region of the suspicious yellow paint that allowed for its identification as a pigment that could not possibly have been used by the purported artist, William Aiken Walker.

Now, let’s take a look at the IR spectrum for 1-hexanol.



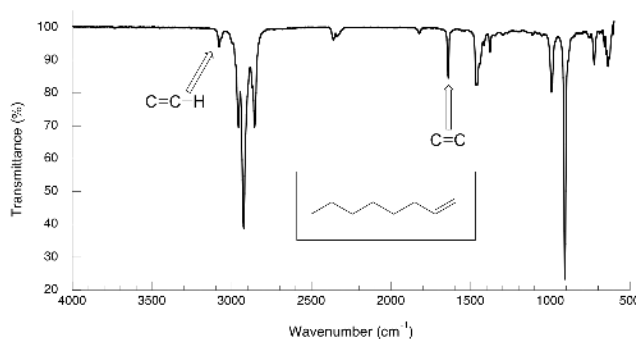
As you can see, the carbonyl peak is gone, and in its place is a very broad ‘mountain’ centered at about 3400 cm^{-1} . This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1} .



We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.

The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm^{-1} is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



Alkynes have characteristic IR absorbance peaks in the range of $2100\text{--}2250\text{ cm}^{-1}$ due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm^{-1} , due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

You can see many more examples of IR spectra in the [Spectral Database for Organic Compounds](#)

Exercise 4.6: Explain how you could use the C-C and C-H stretching frequencies in IR spectra to distinguish between four constitutional isomers: 1,2-dimethylcyclohexene, 1,3-octadiene, 3-octyne, and 1-octyne.

Exercise 4.7: Using the online Spectral Database for Organic Compounds, look up IR spectra for the following compounds, and identify absorbance bands corresponding to those listed in the table above. List actual frequencies for each signal to the nearest cm^{-1} unit, using the information in tables provided on the site.

- 1-methylcyclohexanol
- 4-methylcyclohexene
- 1-hexyne
- 2-hexyne
- 3-hexyne-2,5-diol

Exercise 4.8: A carbon-carbon single bond absorbs in the fingerprint region, and we have already seen the characteristic absorption wavelengths of carbon-carbon double and triple bonds. Rationalize the trend in wavelengths. (*Hint* - remember, we are thinking of bonds as springs, and looking at the frequency at which they 'bounce').

It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in table 1 in the tables section at the end of the text.

As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol (this type of reaction is discussed in detail in [chapter 16](#)).

Kahn Academy video tutorials on infrared spectroscopy

[Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

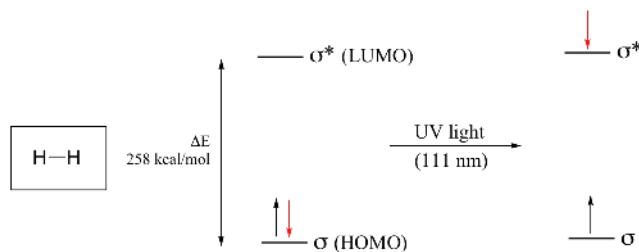
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20.3: Excited Electronic States: Electronic Spectroscopy of Molecules

While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength, higher energy radiation in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum causes many organic molecules to undergo **electronic transitions**. What this means is that when the energy from UV or visible light is absorbed by a molecule, one of its electrons jumps from a lower energy to a higher energy molecular orbital.

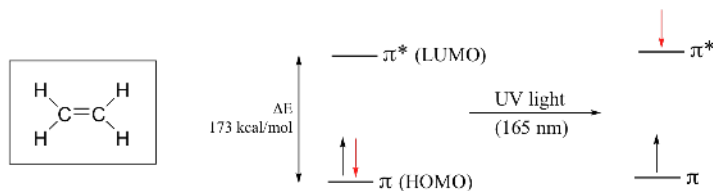
Electronic transitions

Let's take as our first example the simple case of molecular hydrogen, H_2 . As you may recall from section 2.1A, the molecular orbital picture for the hydrogen molecule consists of one bonding σ MO, and a higher energy antibonding σ^* MO. When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ^* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).



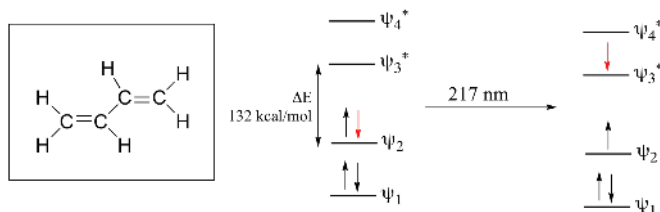
If the molecule is exposed to light of a wavelength with energy equal to ΔE , the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO – in other words, from the σ to the σ^* orbital. This is referred to as a **$\sigma - \sigma^*$ transition**. ΔE for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a **$\pi - \pi^*$ transition**. Because $\pi - \pi^*$ energy gaps are narrower than $\sigma - \sigma^*$ gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



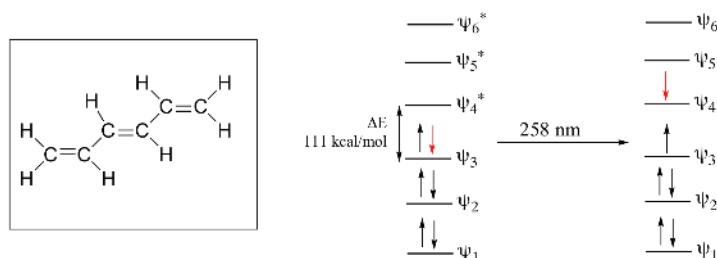
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated π systems. In these groups, the energy gap for $\pi - \pi^*$ transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

Let's revisit the MO picture for 1,3-butadiene, the simplest conjugated system. Recall that we can draw a diagram showing the four π MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are bonding, while the upper two are antibonding.

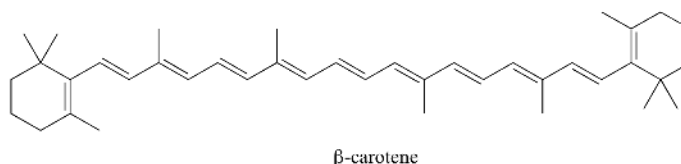


Comparing this MO picture to that of ethene, our isolated pi-bond example, we see that the HOMO-LUMO energy gap is indeed smaller for the conjugated system. 1,3-butadiene absorbs UV light with a wavelength of 217 nm.

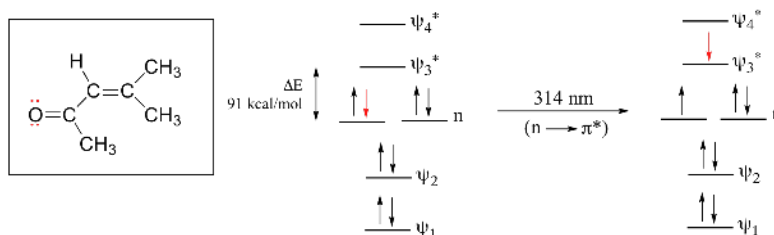
As conjugated pi systems become larger, the energy gap for a $\pi - \pi^*$ transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the $\pi - \pi^*$ transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a ΔE of 111 kcal/mol.



In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather than the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



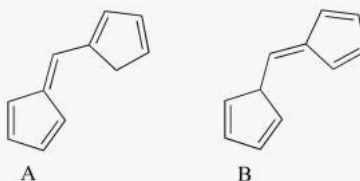
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a $\pi - \pi^*$ transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π^* antibonding MO:



This is referred to as an **$n - \pi^*$ transition**. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an $n \rightarrow \pi^*$ transition is smaller than that of a $\pi - \pi^*$ transition – and thus the $n - \pi^*$ peak is at a longer wavelength. In general, $n - \pi^*$ transitions are weaker (less light absorbed) than those due to $\pi - \pi^*$ transitions.

Exercise 4.9: What is the energy of the photons (in kJ/mol) of light with wavelength of 470 nm, the λ_{max} of b-carotene?

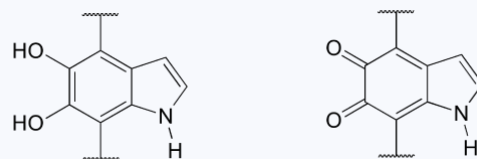
Exercise 4.10: Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.



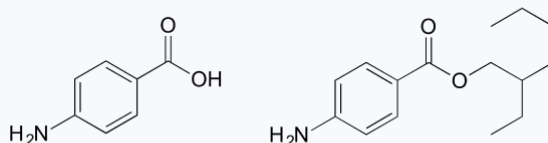
[Solutions](#)

Protecting yourself from sunburn

Human skin can be damaged by exposure to ultraviolet light from the sun. We naturally produce a pigment, called melanin, which protects the skin by absorbing much of the ultraviolet radiation. Melanin is a complex polymer, two of the most common monomers units of which are shown below.



common monomer units in melanin



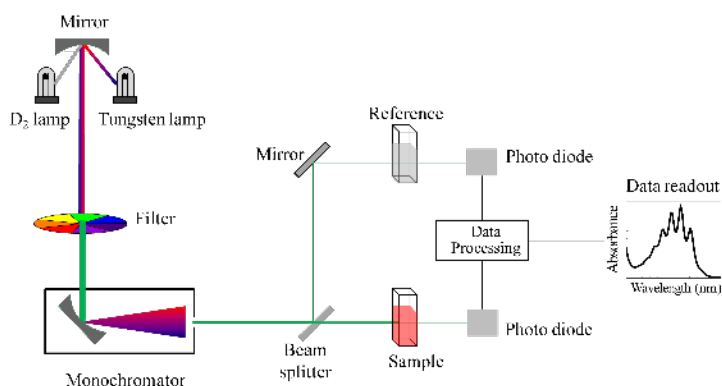
PABA

Padimate-O

Overexposure to the sun is still dangerous, because there is a limit to how much radiation our melanin can absorb. Most commercial sunscreens claim to offer additional protection from both UV-A and UV-B radiation: UV-A refers to wavelengths between 315-400 nm, UV-B to shorter, more harmful wavelengths between 280-315 nm. PABA (*para*-aminobenzoic acid) was used in sunscreens in the past, but its relatively high polarity meant that it was not very soluble in oily lotions, and it tended to rinse away when swimming. Many sunscreens today contain, among other active ingredients, a more hydrophobic derivative of PABA called Padimate O.

Looking at UV-vis spectra

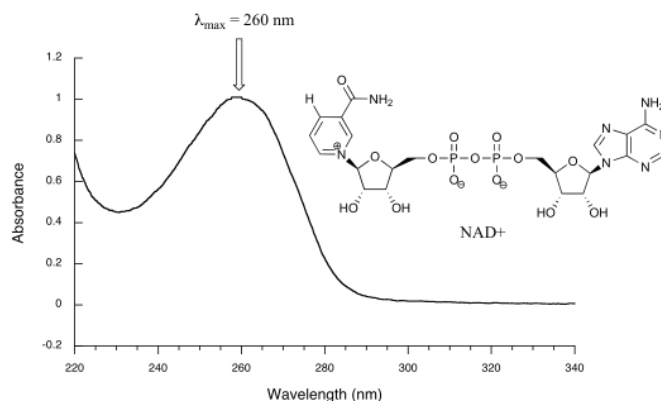
We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred.



Schematic for a UV-Vis spectrophotometer

(Image from [Wikipedia Commons](#))

Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+ . This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



You'll notice that this UV spectrum is much simpler than the IR spectra we saw earlier: this one has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm) rather than in cm^{-1} as is the convention in IR spectroscopy.

Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum. The first is λ_{max} , which is the wavelength at maximal light absorbance. As you can see, NAD⁺ has $\lambda_{\text{max}} = 260 \text{ nm}$. We also want to record how much light is absorbed at λ_{max} . Here we use a unitless number called **absorbance**, abbreviated 'A'. This contains the same information as the 'percent transmittance' number used in IR spectroscopy, just expressed in slightly different terms. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the $\log_{10}$ of that number:

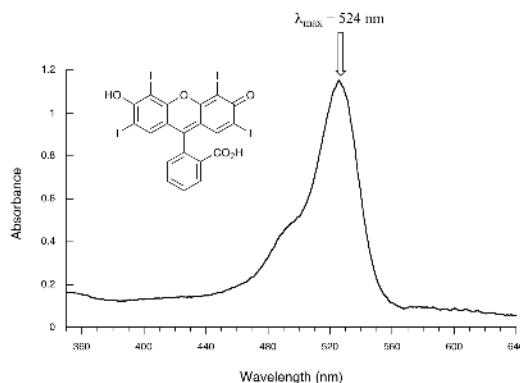
$$A = \log \frac{I_0}{I} \quad (4.3.1)$$

You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

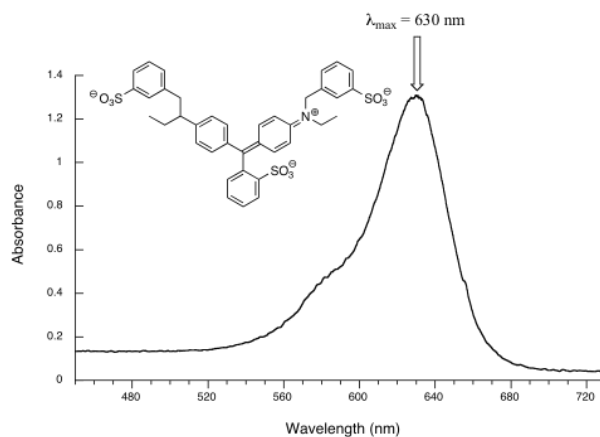
Exercise 4.11: Express $A = 1.0$ in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well).

[Solutions](#)

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes. Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

Applications of UV spectroscopy in organic and biological chemistry

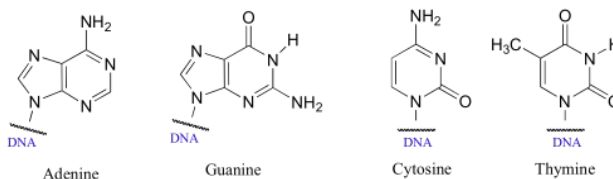
UV-vis spectroscopy has many different applications in organic and biological chemistry. One of the most basic of these applications is the use of the **Beer - Lambert Law** to determine the concentration of a chromophore. You most likely have performed a Beer – Lambert experiment in a previous chemistry lab. The law is simply an application of the observation that, within certain ranges, the absorbance of a chromophore at a given wavelength varies in a linear fashion with its concentration: the higher the concentration of the molecule, the greater its absorbance.

If we divide the observed value of A at $\lambda_{\max}$ by the concentration of the sample (c , in mol/L), we obtain the **molar absorptivity**, or **extinction coefficient** (ϵ), which is a characteristic value for a given compound.

$$\epsilon = \frac{A}{c} \quad (4.3.2)$$

The absorbance will also depend, of course, on the **path length** - in other words, the distance that the beam of light travels through the sample. In most cases, sample holders are designed so that the path length is equal to 1 cm, so the units for molar absorptivity are $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. If we look up the value of ϵ for our compound at $\lambda_{\max}$, and we measure absorbance at this wavelength, we can easily calculate the concentration of our sample. As an example, for NAD^+ the literature value of ϵ at 260 nm is $18,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. In our NAD^+ spectrum we observed $A_{260} = 1.0$, so using equation 4.4 and solving for concentration we find that our sample is $5.6 \times 10^{-5} \text{ M}$.

The bases of DNA and RNA are good chromophores:



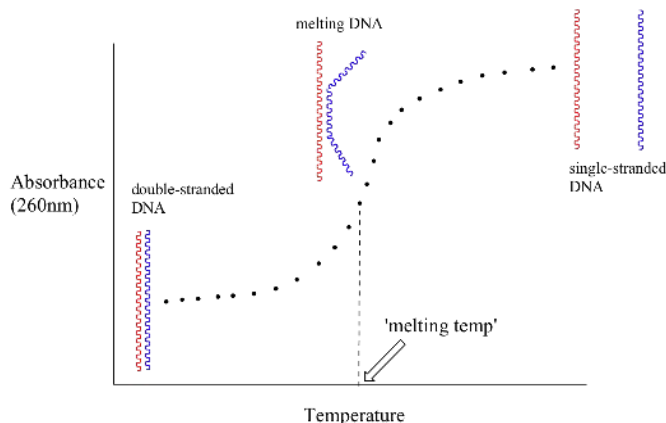
Biochemists and molecular biologists often determine the concentration of a DNA sample by assuming an average value of $\epsilon = 0.020 \text{ ng}^{-1} \cdot \text{mL}$ for double-stranded DNA at its $\lambda_{\max}$ of 260 nm (notice that concentration in this application is expressed in mass/volume rather than molarity: ng/mL is often a convenient unit for DNA concentration when doing molecular biology).

Exercise 4.12: 50 microliters of an aqueous sample of double stranded DNA is dissolved in 950 microliters of water. This diluted solution has a maximal absorbance of 0.326 at 260 nm. What is the concentration of the original (more concentrated) DNA sample, expressed in micrograms per microliter?

[Solutions](#)

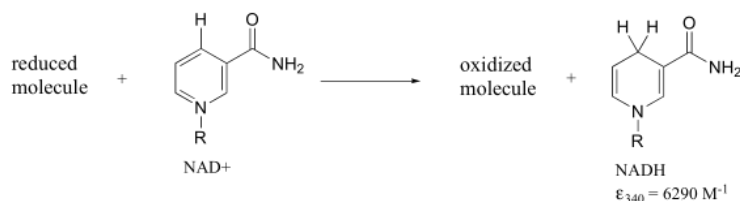
Because the extinction coefficient of double stranded DNA is slightly lower than that of single stranded DNA, we can use UV spectroscopy to monitor a process known as DNA melting. If a short stretch of double stranded DNA is gradually heated up, it will

begin to 'melt', or break apart, as the temperature increases (recall that two strands of DNA are held together by a specific pattern of hydrogen bonds formed by 'base-pairing').

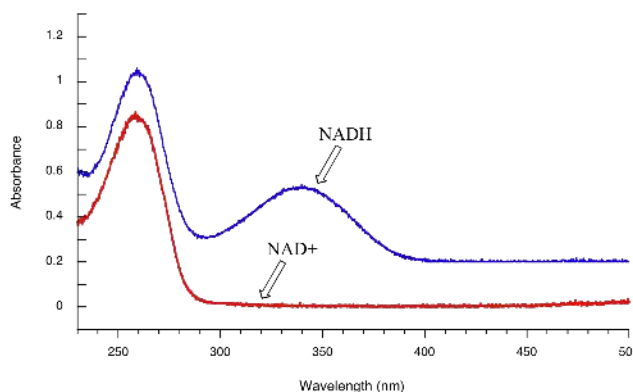


As melting proceeds, the absorbance value for the sample increases, eventually reaching a high plateau as all of the double-stranded DNA breaks apart, or 'melts'. The mid-point of this process, called the 'melting temperature', provides a good indication of how tightly the two strands of DNA are able to bind to each other.

Later we will see how the Beer - Lambert Law and UV spectroscopy provides us with a convenient way to follow the progress of many different enzymatic redox (oxidation-reduction) reactions. In biochemistry, oxidation of an organic molecule often occurs concurrently with reduction of nicotinamide adenine dinucleotide (NAD^+ , the compound whose spectrum we saw earlier in this section) to NADH :

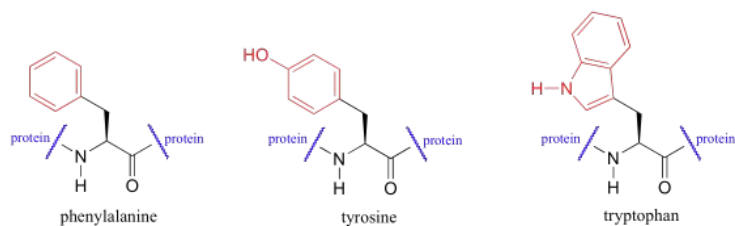


Both NAD^+ and NADH absorb at 260 nm. However NADH , unlike NAD^+ , has a second absorbance band with $\lambda_{\text{max}} = 340 \text{ nm}$ and $\epsilon = 6290 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The figure below shows the spectra of both compounds superimposed, with the NADH spectrum offset slightly on the y-axis:



By monitoring the absorbance of a reaction mixture at 340 nm, we can 'watch' NADH being formed as the reaction proceeds, and calculate the rate of the reaction.

UV spectroscopy is also very useful in the study of proteins. Proteins absorb light in the UV range due to the presence of the aromatic amino acids tryptophan, phenylalanine, and tyrosine, all of which are chromophores.



Biochemists frequently use UV spectroscopy to study conformational changes in proteins - how they change shape in response to different conditions. When a protein undergoes a conformational shift (partial unfolding, for example), the resulting change in the environment around an aromatic amino acid chromophore can cause its UV spectrum to be altered.

Kahn Academy video tutorials on UV-Vis spectroscopy

[Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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