TEN2B-VOLTAGE

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TEN2B-Voltage

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This text was compiled on 01/06/2025

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1: Spontaneity

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1.1: Spontaneous and Nonspontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 1.1.1).

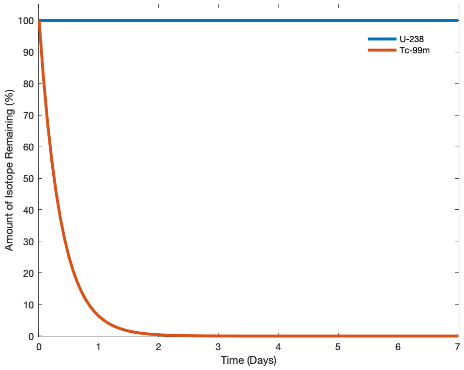

Figure 1.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 1.1.2).

$$\mathrm{C(s, diamond)} \longrightarrow \mathrm{C(s, graphite)} \tag{1.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

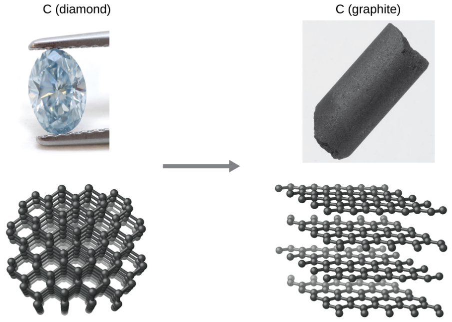

Figure 1.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 1.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{1.1.2}$$

$$= 0 \ \ \mathrm{(P = 0 \ in \ a \ vaccum)} \tag{1.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\begin{aligned}\Delta U &= q + w && \text{(First Law of Thermodynamics)}\\ &= 0 + 0 = 0 && (1.1.4)\end{aligned}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

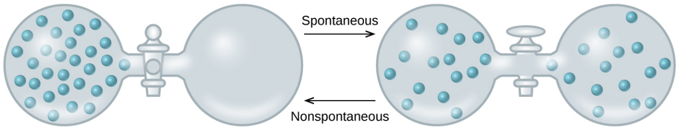

Figure 1.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 1.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{1.1.5}$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

Figure 1.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

✓ Example 1.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

Figure 1.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

? Exercise 1.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process

process that requires continual input of energy from an external source

spontaneous change

process that takes place without a continuous input of energy from an external source

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1.2: Entropy and the Second Law of Thermodynamics

Learning Objectives

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 1.2.1.

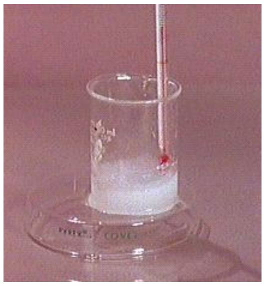

Figure 1.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure $1.2.2$. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

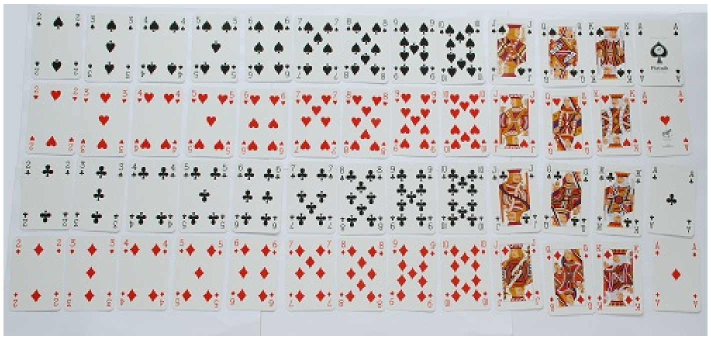

Figure $1.2.2$: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure $1.2.3$). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure $1.2.3$, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

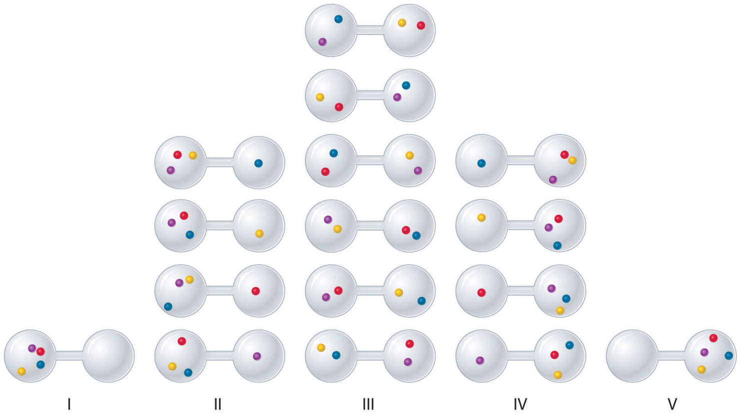

Figure 1.2.3: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

> Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 1.2.4, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

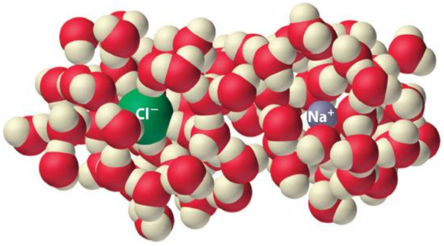

Figure 1.2.4: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

✓ Example 1.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

? Exercise 1.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer a

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

Video Solution

Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum (P_{ext} = 0) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = - P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, ΔU = q + w. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{1.2.1}$$

> Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \text{ and } \Delta S = \frac{q_{\text{rev}}}{T} \tag{1.2.2}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 1.2.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{1.2.3}$$

$$= T\Delta S - P\Delta V \tag{1.2.4}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 1.2.2 and Equation 1.2.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 1.2.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, ΔV > 0, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0.$$

According to Equation 1.2.4, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}.$$

The corresponding change in entropy of the universe is then as follows:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \\ &= 0\end{aligned}$$

Thus no change in ΔS_{univ} has occurred.

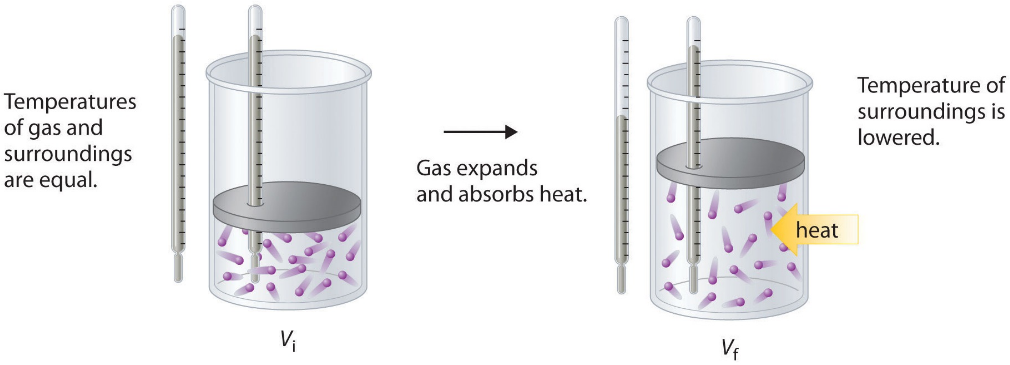

Figure 1.2.5: Expansion of Gas at Constant Temperature

Temperatures of gas and surroundings are equal. Then the gas expands and absorbs heat. Temperature of the surroundings is then lowered.

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 1.2.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 1.2.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

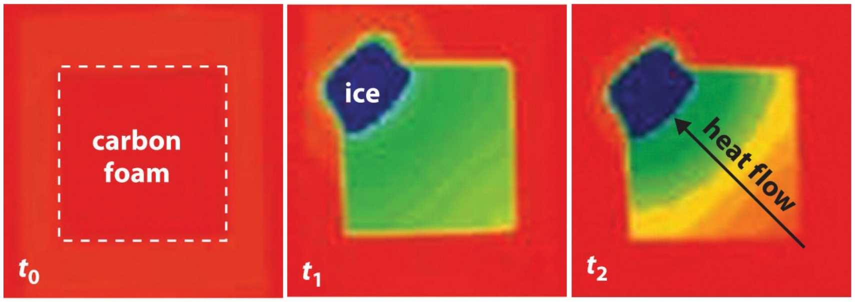

Figure 1.2.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0\ \text{J/(mol•K)} - 22.0\ \text{J/(mol•K)} = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} = \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{1.2.5}$$

The numerators on the right side of Equation 1.2.5 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 1.2.7).

Figure 1.2.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

✓ Example 1.2.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with $\Delta H = -2.1$ kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 1.2.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 1.2.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

Video 1.2.1 : *Time lapse tin pest reaction.*

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)

? Exercise 1.2.2

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α

Entropy: Entropy(opens in new window) [youtu.be]

Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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1.3: Entropy Changes Associated with State Changes

Phase Changes

When a system receives an amount of energy q at a constant temperature, T, the entropy increase ΔS is defined by the following equation. Hence, the magnitude of ΔS for a reversible process such as a phase change is calculated

$$\Delta S=\frac{q_{rev}}{T} \tag{1.3.1}$$

with the temperature in Kelvin. Since entropy changes are much smaller than enthalpy changes, they are usually reported in J K^{-1} mol^{-1}.

Examples of reversible processes are

- **Boiling:** As temperature is constant,

$$\Delta S=\frac{\Delta H_{vap}}{T} \tag{1.3.2}$$

- **Melting:** As temperature is constant,

$$\Delta S=\frac{\Delta H_{fus}}{T} \tag{1.3.3}$$

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are significantly more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}}+\Delta S_{\text{surr}} \\ &= \Delta S_{\text{sys}}+\frac{q_{\text{surr}}}{T}\end{aligned} \tag{1.3.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 1.3.1.

✓ Example 1.3.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s)\longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{sys}=22.1\ J/K$ and $q_{surr}=-6.00\ kJ$.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}}+\Delta S_{\text{surr}} \\ &= \Delta S_{\text{sys}}+\frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K+\frac{-6.00\times 10^3\ J}{263.15\ K} \\ &= -0.7\ J/K\end{aligned}$$

Since $S_{univ}<0$, melting is nonspontaneous (*not* spontaneous) at **−10.0 °C**.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} \\ &= +0.9\ J/K\end{aligned}$$

Since $S_{univ} > 0$, melting of ice *is* spontaneous at **10.00 °C.**

Example 1.3.2

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

Ice Melting

Ice melting provides an example in which entropy increases in a small system, a thermodynamic system consisting of the surroundings (the warm room) and the entity of glass container, ice, water which has been allowed to reach thermodynamic equilibrium at the melting temperature of ice. In this system, some heat (*δQ*) from the warmer surroundings at 298 K (25 °C; 77 °F) transfers to the cooler system of ice and water at its constant temperature (*T*) of 273 K (0 °C; 32 °F), the melting temperature of ice. The entropy of the system, which is *δQ/T*, increases by *δQ/273K*. The heat *δQ* for this process is the energy required to change water from the solid state to the liquid state, and is called the enthalpy of fusion, i.e. *ΔH* for ice fusion.

It is important to realize that the entropy of the surrounding room decreases less than the entropy of the ice and water increases: the room temperature of 298 K is larger than 273 K and therefore the ratio, (entropy change), of *δQ/298K* for the surroundings is smaller than the ratio (entropy change), of *δQ/273K* for the ice and water system. This is always true in spontaneous events in a thermodynamic system and it shows the predictive importance of entropy: the final net entropy after such an event is always greater than was the initial entropy.

As the temperature of the cool water rises to that of the room and the room further cools imperceptibly, the sum of the *δQ/T* over the continuous range, “at many increments”, in the initially cool to finally warm water can be found by calculus. The entire miniature ‘universe’, i.e. this thermodynamic system, has increased in entropy. Energy has spontaneously become more dispersed and spread out in that ‘universe’ than when the glass of ice and water was introduced and became a 'system' within it.

Example 1.3.3

Calculate entropy change when 36.0 g of ice melts at 273 K and 1 atm.

Solution

This is a directly application of Equation 1.3.3, which requires the enthalpy of fusion for this reaction and the temperature is already given. If you look up the enthalpy of fusion for ice, you would get a molar enthalpy of 6.01 kJ/mol.

$$\Delta S = \left(\frac{6.01\, kJ\, mol^{-1}}{273\ K}\right)$$

This is a molar value that needs to be scaled by the amount of the material (36 g). So a standard mass-to-moles conversion factor is needed (along with the molar mass of water - 18.01 g/mol).

$$\begin{aligned}\Delta S &= \left(\frac{6.01\, kJ\ \cancel{mol^{-1}}}{273\ K}\right)\left(\frac{36\ \cancel{g}}{18.01\ \cancel{g}\ \cancel{mol^{-1}}}\right) \\ &= 0.044\, kJ/K\end{aligned}$$

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1.4: Heat Transfer and Changes in the Entropy of the Surroundings

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1.5: Entropy Changes in Chemical Reactions

Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at °0C at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

$$\mathrm{H_2O(s)} \rightarrow \mathrm{H_2O(l)} \tag{1.5.1}$$

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

> *However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)*

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

Standard Molar Entropy, S^0

The entropy of a substance has an absolute value of 0 entropy at 0 K.

- **Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in Table T2.
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the *n*, and *m*, terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^0 = \sum_n nS^0(products) - \sum_m mS^0(reactants)$$

Example 1.5.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

At 298K as a standard temperature:

- $S^0(NH_3)$ = 192.5 J/mol K
- $S^0(H_2)$ = 130.6 J/mol K
- $S^0(N_2)$ = 191.5 J/mol K

Solution

From the balanced equation we can write the equation for ΔS^0 (the change in the standard molar entropy for the reaction):

$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$

$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$

$\Delta S^0 = -198.3$ J/mol K

It would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the $N_2(g)$ used to float around independently of the H_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar “products minus reactants” rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 1.5.2 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

> ΔS° for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate ΔH°.

✓ Example 1.5.2: Combustion of Octane

Use the data in Table T2 to calculate ΔS° for the combustion reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table T2. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$\mathrm{C_8H_{18}(l) + \tfrac{25}{2}\,O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)}$$

We calculate ΔS° for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \\ &= [8S^\circ(\mathrm{CO_2}) + 9S^\circ(\mathrm{H_2O})] - [S^\circ(\mathrm{C_8H_{18}}) + \frac{25}{2}S^\circ(\mathrm{O_2})] \\ &= \{[8\text{ mol CO}_2 \times 213.8\text{ J}/(\text{mol}\cdot\text{K})] + [9\text{ mol H}_2\text{O} \times 188.8\text{ J}/(\text{mol}\cdot\text{K})]\} \\ &\quad - \left\{[1\text{ mol C}_8\text{H}_{18} \times 329.3\text{ J}/(\text{mol}\cdot\text{K})] + \left[\frac{25}{2}\text{ mol O}_2 \times 205.2\text{ J}/(\text{mol}\cdot\text{K})\right]\right\} \\ &= 515.3\text{ J}/\text{K}\end{aligned}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 1.5.2

Use the data in Table T2 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer

−361.1 J/K

Calculating the Entropy of Reaction using S: Calculating the Entropy of Reaction using S(opens in new window) [youtu.be]

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CHAPTER OVERVIEW

2: Gibbs Energy

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2.1: Gibbs Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{2.1.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{2.1.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 2.1.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{2.1.3}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{2.1.4}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{2.1.5}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 2.1.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 2.1.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 2.1.3), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657 \text{ J}}{373.15 \text{ K}} \\ &= 108.96 \text{ J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657 \text{ J} - [(373.15 \text{ K})(108.96 \text{ J/K})] \\ &= 0 \text{ J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657 \text{ J} - [(383.15 \text{ K})(108.96 \text{ J/K})] \\ &= -1091 \text{ J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\text{ J} - [(363.15\text{ K})(108.96\text{ J/K})] \\ &= 1088\text{ J}\end{aligned}$$

At 90°C, $\Delta G > 0$, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110°C} = 1090\text{ J} = -\Delta G_{90°C}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 2.1.2), setting $\Delta G = 0$, and solving for T,

$$0\text{ J}=40{,}657\text{ J}-T(108.96\text{ J/K})$$
$$T=373.15\text{ K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 2.1.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

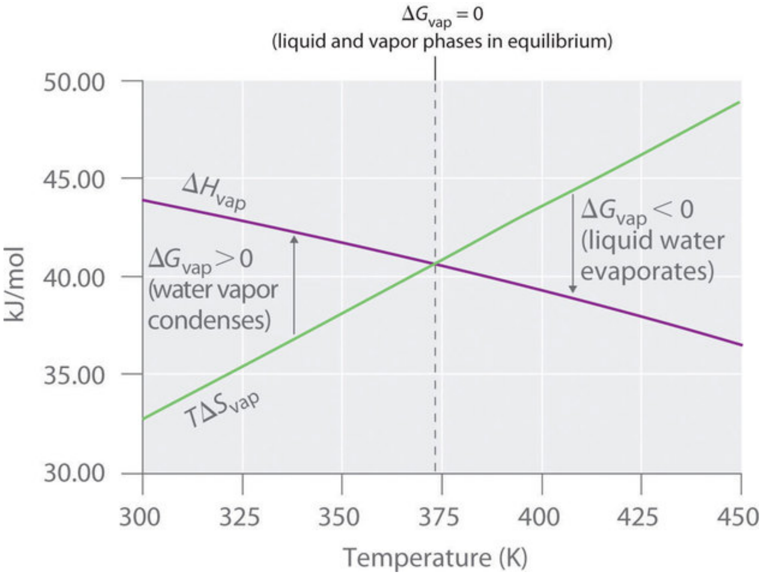

Figure 2.1.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Definition of Gibbs Free Energy: The Definition of Gibbs Free Energy (opens in new window) [youtu.be]

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 2.1.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{2.1.6}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 2.1.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 2.1.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30

Device	Energy Conversion	Approximate Efficiency (%)
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 2.1.7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.1.7}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

✓ Example 2.1.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 2.1.7, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1 \text{ mol } \mathrm{H_2O_2} \times 109.6 \text{ J}/(\text{mol}\cdot\text{K})] \\ &\quad - \{[1 \text{ mol } \mathrm{H_2} \times 130.7 \text{ J}/(\text{mol}\cdot\text{K})] + [1 \text{ mol } \mathrm{O_2} \times 205.2 \text{ J}/(\text{mol}\cdot\text{K})]\} \\ &= -226.3 \text{ J/K (per mole of } \mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 2.1.7,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol} \end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

? Exercise 2.1.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Answer

149.5 kJ/mol

no, not spontaneous

Video Solution

Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be] (opens in new window)

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^\circ_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{2.1.8}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta^o_f(reactants) \tag{2.1.9}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 2.1.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(l)}$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, ΔG°_f (O_2) is zero. Using the “products minus reactants” rule,

$$\begin{aligned} \Delta G^\circ &= [8\Delta G^\circ_f(\mathrm{CO_2}) + 9\Delta G^\circ_f(\mathrm{H_2O})] - \left[1\Delta G^\circ_f(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_f(\mathrm{O_2})\right] \\ &= [(8\ \mathrm{mol})(-394.4\ \mathrm{kJ/mol}) + (9\ \mathrm{mol})(-237.1\ \mathrm{kJ/mol})] \\ &\quad - \left[(1\ \mathrm{mol})(-353.2\ \mathrm{kJ/mol}) + \left(\frac{25}{2}\ \mathrm{mol}\right)(0\ \mathrm{kJ/mol})\right] \\ &= -4935.9\ \mathrm{kJ\ (per\ mol\ of\ C_8H_{18})} \end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 2.1.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Video Solution

Calculating Grxn using Gf: Calculating Grxn using Gf(opens in new window) [youtu.be]

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

> In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 2.1.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- $\Delta H^\circ_f (NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that $\Delta H^\circ{}_f$ for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 2.1.7 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 2.1.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 2.1.7, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J}/(\text{mol}\cdot\text{K})] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J}/(\text{mol}\cdot\text{K})] + [3\text{ mol H}_2 \times 130.7\text{ J}/(\text{mol}\cdot\text{K})]\} \\ &= -198.1\text{ J/K (per mole of N}_2)\end{aligned} \tag{2.1.10}$$

We can also calculate ΔH° for the reaction using the “products minus reactants” rule. The value of $\Delta H^\circ{}_f$ (NH_3) is given, and $\Delta H^\circ{}_f$ is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of N}_2)\end{aligned}$$

B Inserting the appropriate values into Equation 2.1.7

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2)$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 2.1.2:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of N}_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 2.1.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),

- S°(NO_2) = 240.1 J/(mol•K),
- ΔH˚$_f$(NO_2) = 33.2 kJ/mol, and
- ΔH˚$_f$ (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 2.1.7, as illustrated in Example 2.1.4.

✓ Example 2.1.4

As you saw in Example 2.1.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 2.1.7 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 2.1.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG° = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 2.1.7 to solve for T:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T = \frac{\Delta H^\circ}{\Delta S^\circ} &= \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}\end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

? Exercise 2.1.4

As you found in the exercise in Example 2.1.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Video Solution

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

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

- Standard free-energy change:

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

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, $\Delta G = 0$. If the process is spontaneous, $\Delta G < 0$. If the process is not spontaneous as written but is spontaneous in the reverse direction, $\Delta G > 0$. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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2.2: Gibbs Energy Changes in Chemical Reactions

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{2.2.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled "On the Equilibrium of Heterogeneous Substances" was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{2.2.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 2.2.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\mathrm{surr}}=-\frac{\Delta H_{\mathrm{sys}}}{T} \tag{2.2.3}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ}>0$, so substituting we obtain

$$\begin{aligned}\Delta S_{\text{univ }} &=\Delta S_{\text{sys}}+\Delta S_{\text{surr}}>0 \qquad (2.2.4)\\ &=\Delta S_{\text{sys}}-\frac{\Delta H_{\text{sys}}}{T}>0 \qquad (2.2.5)\end{aligned}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys}-T\Delta S_{sys}<0$$

which is equal to ΔG (Equation 2.2.2). We can therefore see that for a spontaneous process, $\Delta G<0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 2.2.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys}\gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G<0$, the process occurs spontaneously.
- If $\Delta G=0$, the system is at equilibrium.
- If $\Delta G>0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H=40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 2.2.3), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &=\frac{\Delta H_{\text{vap}}}{T_{\text{b}}}\\ &=\frac{\text{40,657 J}}{\text{373.15 K}}\\ &=108.96\text{ J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &=\Delta H_{100^\circ\text{C}}-T\Delta S_{100^\circ\text{C}}\\ &=\text{40,657 J}-[(373.15\text{ K})(108.96\text{ J/K})]\\ &=0\text{ J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &=\Delta H-T\Delta S\\ &=\text{40,657 J}-[(383.15\text{ K})(108.96\text{ J/K})]\\ &=-1091\text{ J}\end{aligned}$$

At 110°C, $\Delta G<0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\text{ J} - [(363.15\text{ K})(108.96\text{ J/K})] \\ &= 1088\text{ J}\end{aligned}$$

At 90°C, $\Delta G > 0$, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C} = 1090\text{ J} = -\Delta G_{90^\circ C}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 2.2.2), setting $\Delta G = 0$, and solving for T,

$$0\text{ J}=40{,}657\text{ J}-T(108.96\text{ J/K})$$
$$T=373.15\text{ K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 2.2.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

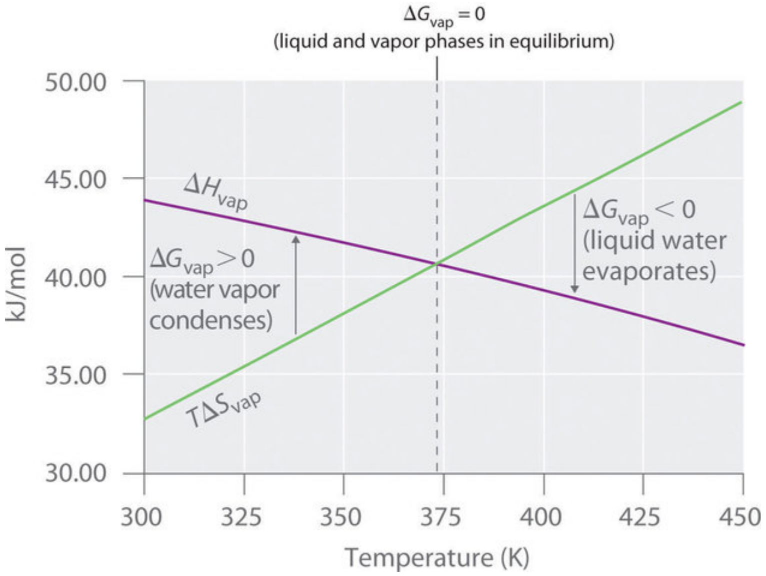

Figure 2.2.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Definition of Gibbs Free Energy: The Definition of Gibbs Free Energy (opens in new window) [youtu.be]

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let’s look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 2.2.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{2.2.6}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 2.2.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 2.2.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30

Device	Energy Conversion	Approximate Efficiency (%)
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 2.2.7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.2.7}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

✓ Example 2.2.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 2.2.7, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned} \Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \mathrm{mol\ H_2O_2} \times 109.6\ \mathrm{J/(mol\cdot K)}] \\ &\quad - \{[1\ \mathrm{mol\ H_2} \times 130.7\ \mathrm{J/(mol\cdot K)}] + [1\ \mathrm{mol\ O_2} \times 205.2\ \mathrm{J/(mol\cdot K)}]\} \\ &= -226.3\ \mathrm{J/K}\ (\text{per mole of } \mathrm{H_2O_2}) \end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 2.2.7,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol\cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

? Exercise 2.2.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Answer

149.5 kJ/mol

no, not spontaneous

Video Solution

Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be] (opens in new window)

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^\circ_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{2.2.8}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta^o_f(reactants) \tag{2.2.9}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 2.2.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(l)}$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, ΔG°_f (O_2) is zero. Using the “products minus reactants” rule,

$$\begin{aligned} \Delta G^\circ &= [8\Delta G^\circ_\mathrm{f}(\mathrm{CO_2}) + 9\Delta G^\circ_\mathrm{f}(\mathrm{H_2O})] - \left[1\Delta G^\circ_\mathrm{f}(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_\mathrm{f}(\mathrm{O_2})\right] \\ &= [(8\ \mathrm{mol})(-394.4\ \mathrm{kJ/mol}) + (9\ \mathrm{mol})(-237.1\ \mathrm{kJ/mol})] \\ &\quad - \left[(1\ \mathrm{mol})(-353.2\ \mathrm{kJ/mol}) + \left(\frac{25}{2}\ \mathrm{mol}\right)(0\ \mathrm{kJ/mol})\right] \\ &= -4935.9\ \mathrm{kJ}\ (\text{per mol of }\mathrm{C_8H_{18}}) \end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 2.2.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Video Solution

Calculating Grxn using Gf: Calculating Grxn using Gf(opens in new window) [youtu.be]

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

> In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 2.2.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 2.2.7 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 2.2.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 2.2.7, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{\mathrm{rxn}} &= 2S^\circ(\mathrm{NH_3}) - [S^\circ(\mathrm{N_2}) + 3S^\circ(\mathrm{H_2})]\\ &= [2\text{ mol NH}_3 \times 192.8\text{ J/(mol}\cdot\text{K)}]\\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol H}_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\}\\ &= -198.1\text{ J/K (per mole of N}_2)\end{aligned} \tag{2.2.10}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\mathrm{rxn}} &= 2\Delta H^\circ_f(\mathrm{NH_3}) - [\Delta H^\circ_f(\mathrm{N_2}) + 3\Delta H^\circ_f(\mathrm{H_2})]\\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})]\\ &= -91.8\text{ kJ(per mole of N}_2)\end{aligned}$$

B Inserting the appropriate values into Equation 2.2.7

$$\Delta G^\circ_{\mathrm{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2)$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 2.2.2:

$$\begin{aligned}\Delta G_{300^\circ\mathrm{C}} &= \Delta H_{300^\circ\mathrm{C}} - (573\text{ K})(\Delta S_{300^\circ\mathrm{C}})\\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ\\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J})\\ &= 21.7\text{ kJ (per mole of N}_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 2.2.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)}$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),

- S°(NO_2) = 240.1 J/(mol•K),
- ΔH$^\circ_f$(NO_2) = 33.2 kJ/mol, and
- ΔH$^\circ_f$ (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 2.2.7, as illustrated in Example 2.2.4.

✓ Example 2.2.4

As you saw in Example 2.2.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 2.2.7 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 2.2.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG° = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 2.2.7 to solve for T:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T = \frac{\Delta H^\circ}{\Delta S^\circ} &= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K} \end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

? Exercise 2.2.4

As you found in the exercise in Example 2.2.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Video Solution

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

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

- Standard free-energy change:

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

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, $\Delta G = 0$. If the process is spontaneous, $\Delta G < 0$. If the process is not spontaneous as written but is spontaneous in the reverse direction, $\Delta G > 0$. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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2.3: Gibbs Energy Changers for Non-Standard States

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table $2.3.1$ summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 2.3.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{2.3.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 2.3.1 simplifies to

$$\Delta G = V\Delta P \tag{2.3.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 2.3.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{2.3.3}$$

$$= nRT\frac{\Delta P}{P} \tag{2.3.4}$$

$$= nRT\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{2.3.5}$$

If the initial state is the standard state with $P_i = 1\,atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{2.3.6}$$

As you will soon discover, Equation 2.3.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{2.3.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{2.3.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{2.3.9}$$

Substituting Equation 2.3.6 for each term into Equation 2.3.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P^c_{\text{C}} P^d_{\text{D}}}{P^a_{\text{A}} P^b_{\text{B}}} \right) \tag{2.3.10}$$

$$= \Delta G^\circ + RT \ln Q \tag{2.3.11}$$

where ΔG^o indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^o + RT \ln K_p \tag{2.3.12}$$

$$\Delta G^o = -RT \ln K_p \tag{2.3.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

✓ Example 2.3.1

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

$$\text{N}_2(\text{g}) + 3\,\text{H}_2(\text{g}) \rightleftharpoons 2\,\text{NH}_3(\text{g})$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm, and
- $T = 100^o C$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 2.3.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 2.3.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 2.3.11. Substituting the partial pressures given, we can calculate Q:

$$\begin{aligned} Q &= \frac{P^2_{\mathrm{NH_3}}}{P_{\mathrm{N_2}} P^3_{\mathrm{H_2}}} \\ &= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7} \end{aligned}$$

B Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 2.3.11,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of } \mathrm{N_2} \end{aligned}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 2.3.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✓ Example 2.3.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 2.3.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 2.3.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 2.3.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 2.3.13,

$$\begin{aligned}\Delta G^\circ &= -RT\ln K_\mathrm{p} \\ \frac{-\Delta G^\circ}{RT} &= \ln K_\mathrm{p}\end{aligned}$$

Inserting the value of ΔG^o and the temperature (25°C = 298 K) into this equation,

$$\begin{aligned}\ln K_\mathrm{p} &= -\frac{(-32.7\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298\ \mathrm{K})} = 13.2 \\ K_\mathrm{p} &= 5.4\times 10^5\end{aligned}$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 2.3.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{2.3.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 2.3.13 can be written in a more general form:

$$\Delta G^\circ = -RT\ln K \tag{2.3.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 2.3.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 2.3.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.3.16}$$

$$= -RT\ln K \tag{2.3.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*

Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 2.3.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{2.3.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 2.3.18 agrees with the qualitative predictions made by applying Le Chatelier’s principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 2.3.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 2.3.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.3.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

Example 2.3.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 2.3.3. What is K_p at 500°C? (Use the data from Example 2.3.1.)

Given: balanced chemical equation, $\Delta H^{o\circ}$, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 2.3.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^o for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 2.3.19 we obtain the following:

$$\begin{aligned} \ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \\ &= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{8.314 \text{ J/K}}\left(\frac{1}{298 \text{ K}}-\frac{1}{773 \text{ K}}\right) = -22.8 \\ \frac{K_2}{K_1} &= 1.3 \times 10^{-10} \\ K_2 &= (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5} \end{aligned}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 2.3.4

In the exercise in Example 2.3.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH^o_f values in the exercise in Example 2.3.1 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG^o < 0, then K > 1, and products are favored over reactants at equilibrium. Conversely, if ΔG^o > 0, then K < 1, and reactants are favored over products at equilibrium. If ΔG^o = 0, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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2.4: Gibbs Energy and Equilibrium

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table $2.4.1$ summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table $2.4.1$: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{2.4.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 2.4.1 simplifies to

$$\Delta G = V\Delta P \tag{2.4.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 2.4.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{2.4.3}$$

$$= nRT\frac{\Delta P}{P} \tag{2.4.4}$$

$$= nRT\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{2.4.5}$$

If the initial state is the standard state with $P_i = 1\,atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^{\circ} = nRT\ln P$$

This can be rearranged as follows:

$$G = G^{\circ} + nRT\ln P \tag{2.4.6}$$

As you will soon discover, Equation 2.4.6 allows us to relate ΔG^{o} and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{2.4.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{2.4.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{2.4.9}$$

Substituting Equation 2.4.6 for each term into Equation 2.4.9,

$$\Delta G = [(cG^{o}_{C} + cRT\ln P_C) + (dG^{o}_{D} + dRT\ln P_D)] - [(aG^{o}_{A} + aRT\ln P_A) + (bG^{o}_{B} + bRT\ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^{\circ} + RT\ln\left(\frac{P^{c}_{\mathrm{C}}P^{d}_{\mathrm{D}}}{P^{a}_{\mathrm{A}}P^{b}_{\mathrm{B}}}\right) \tag{2.4.10}$$

$$= \Delta G^{\circ} + RT\ln Q \tag{2.4.11}$$

where ΔG^{o} indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^{o} and K_p for gases as follows:

$$0 = \Delta G^{o} + RT\ln K_p \tag{2.4.12}$$

$$\Delta G^{o} = -RT\ln K_p \tag{2.4.13}$$

If the products and reactants are in their standard states and $\Delta G^{o} < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^{o} > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^{o} = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

✓ Example 2.4.1

ΔG^{o} is −32.7 kJ/mol of N_2 for the reaction

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm, and
- $T = 100^{o}C$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 2.4.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 2.4.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 2.4.11. Substituting the partial pressures given, we can calculate Q:

$$\begin{aligned} Q &= \frac{P^2_{\mathrm{NH_3}}}{P_{\mathrm{N_2}} P^3_{\mathrm{H_2}}} \\ &= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7} \end{aligned}$$

B Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 2.4.11,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of } \mathrm{N_2} \end{aligned}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 2.4.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✓ Example 2.4.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 2.4.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 2.4.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 2.4.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 2.4.13,

$$\begin{aligned}\Delta G^\circ &= -RT\ln K_\mathrm{p}\\ \frac{-\Delta G^\circ}{RT} &= \ln K_\mathrm{p}\end{aligned}$$

Inserting the value of ΔG^o and the temperature (25°C = 298 K) into this equation,

$$\begin{aligned}\ln K_\mathrm{p} &= -\frac{(-32.7\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298\ \mathrm{K})} = 13.2\\ K_\mathrm{p} &= 5.4\times 10^5\end{aligned}$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 2.4.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{2.4.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 2.4.13 can be written in a more general form:

$$\Delta G^\circ = -RT\ln K \tag{2.4.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 2.4.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 2.4.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.4.16}$$

$$= -RT\ln K \tag{2.4.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*

Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 2.4.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{2.4.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 2.4.18 agrees with the qualitative predictions made by applying Le Chatelier’s principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 2.4.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 2.4.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.4.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

✓ Example 2.4.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 2.4.3. What is K_p at 500°C? (Use the data from Example 2.4.1.)

Given: balanced chemical equation, $\Delta H^{o\circ}$, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 2.4.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^o for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 2.4.19 we obtain the following:

$$\begin{aligned}\ln\frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\\ &= \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{8.314\text{ J/K}}\left(\frac{1}{298\text{ K}}-\frac{1}{773\text{ K}}\right) = -22.8\\ \frac{K_2}{K_1} &= 1.3\times10^{-10}\\ K_2 &= (5.4\times10^5)(1.3\times10^{-10}) = 7.0\times10^{-5}\end{aligned}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

? Exercise 2.4.4

In the exercise in Example 2.4.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH^o_f values in the exercise in Example 2.4.1 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG^o < 0, then K > 1, and products are favored over reactants at equilibrium. Conversely, if ΔG^o > 0, then K < 1, and reactants are favored over products at equilibrium. If ΔG^o = 0, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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CHAPTER OVERVIEW

3: Potential

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3.1: Balancing Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of Cr^{2+}(aq) with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 3.1.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{\mathrm{Cr}}{}^{2+}(aq) + \overset{+4}{\mathrm{Mn}}\overset{-2}{\mathrm{O}}{}_2(aq) + \overset{+1}{\mathrm{H}}{}^{+}(aq) \rightarrow \overset{+3}{\mathrm{Cr}}{}^{3+}(aq) + \overset{+2}{\mathrm{Mn}}{}^{2+}(aq) + \overset{+1}{\mathrm{H}}{}_2\overset{-2}{\mathrm{O}}(l) \tag{3.1.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$\mathrm{Cr^{2+} + Mn^{4+} \longrightarrow Cr^{3+} + Mn^{2+}} \tag{3.1.2}$$

The oxidation can be written as

$$\underbrace{\mathrm{Cr^{2+} \longrightarrow Cr^{3+} + e^-}}_{\text{oxidation with 1 electron lost}} \tag{3.1.3}$$

and the reduction as

$$\underbrace{\mathrm{Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}}}_{\text{reduction with 2 electrons gained}} \tag{3.1.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 3.1.3) by 2 to give

$$\mathrm{2\,Cr^{2+} \longrightarrow 2\,Cr^{3+} + 2\,e^-} \tag{3.1.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 3.1.4):

$$\mathrm{2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + 2\,e^-}$$

$$\mathrm{Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$\mathrm{2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + 2\,\cancel{e^-}}$$

$$\mathrm{Mn^{4+} + 2\,\cancel{e^-} \rightarrow Mn^{2+}}$$

to result in the balanced redox reaction (metals only)

$$\mathrm{Mn^{4+} + 2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + Mn^{2+}} \tag{3.1.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$\mathrm{MnO_2(aq) + 2\,Cr^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq)} \tag{3.1.7}$$

> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 3.1.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add H^+ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding OH^- as necessary to either side of the equation to balance the charges.

In this case, adding four H^+ ions to the left side of Equation 3.1.7 to give

$$\mathrm{MnO_2(s) + 2\,Cr^{2+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq)} \tag{3.1.8}$$

Although the charges are now balanced in Equation 3.1.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding H_2O as necessary to either side of the equation. Here, we need to add two H_2O molecules to the right side of Equation 3.1.8:

$$\mathrm{MnO_2(s) + 2\,Cr^{2+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq) + 2\,H_2O(l)} \tag{3.1.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 3.1.1 below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding H_2O molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

✓ Example 3.1.1: Balancing in Acid Solutions

Arsenic acid (H_3AsO_4) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine (AsH_3, a highly toxic and unstable gas) and $Zn^{2+}(aq)$. Balance the equation for this reaction using oxidation states:

$$\mathrm{H_3AsO_4(aq) + Zn(s) \longrightarrow AsH_3(g) + Zn^{2+}(aq)}$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.
2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$H_3\overset{+5}{As}O_4(aq)+\overset{0}{Zn}(s)\rightarrow \overset{-3}{As}H_3(g)+\overset{+2}{Zn}{}^{2+}(aq)$$

3. *Write separate equations for oxidation and reduction.* The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{As}+8e^-\rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Zn}\rightarrow \overset{+2}{Zn}{}^{2+}+2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\overset{+5}{\mathrm{As}}+8\,\mathrm{e^-}\rightarrow \overset{-3}{\mathrm{As}}$$

$$4\,\overset{0}{\mathrm{Zn}}\rightarrow 4\,\overset{+2}{\mathrm{Zn}}{}^{2+}+8\,\mathrm{e^-}$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives
   - Reduction:

$$\mathrm{H_3AsO_4(aq)+8\,e^-\rightarrow AsH_3(g)}$$

   - Oxidation:

$$\mathrm{4\,Zn(s)\longrightarrow 4\,Zn^{2+}(aq)+8\,e^-}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$\mathrm{H_3AsO_4(aq)+4\,Zn(s)+\cancel{8\,e^-}\rightarrow AsH_3(g)+4\,Zn^{2+}(aq)+\cancel{8\,e^-}}$$

which then yields after canceling electrons

$$\mathrm{H_3AsO_4(aq)+4\,Zn(s)\rightarrow AsH_3(g)+4\,Zn^{2+}(aq)}$$

7. *Balance the charge by adding $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$\mathrm{H_3AsO_4(aq)+4\,Zn(s)+8\,H^+(aq)\rightarrow AsH_3(g)+4\,Zn^{2+}(aq)}$$

8. *Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 $\mathrm{H_2O}$ molecules to the right side balances the O atoms:

$$\mathrm{H_3AsO_4(aq)+4\,Zn(s)+8\,H^+(aq)\rightarrow AsH_3(g)+4\,Zn^{2+}(aq)+4\,H_2O(l)}$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
   - Atoms:

$$1\,\mathrm{As}+4\,\mathrm{Zn}+4\,\mathrm{O}+11\,\mathrm{H}\overset{\checkmark}{=}1\,\mathrm{As}+4\,\mathrm{Zn}+4\,\mathrm{O}+11\,\mathrm{H}$$

   - Charge:

$$8(+1)\overset{\checkmark}{=}4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$\mathrm{H_3AsO_4(aq)}+4\,\mathrm{Zn(s)}+8\,\mathrm{H^+(aq)}\longrightarrow\mathrm{AsH_3(g)}+4\,\mathrm{Zn^{2+}(aq)}+4\,\mathrm{H_2O(l)}$$

? Exercise 3.1.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$\mathrm{CuS(s)}+\mathrm{H^+(aq)}+\mathrm{NO_3^-(aq)}\longrightarrow\mathrm{Cu^{2+}(aq)}+\mathrm{NO(g)}+\mathrm{SO_4^{2-}(aq)}$$

Answer

$$3\,\mathrm{CuS(s)}+8\,\mathrm{H^+(aq)}+8\,\mathrm{NO_3^-(aq)}\rightarrow3\,\mathrm{Cu^{2+}(aq)}+8\,\mathrm{NO(g)}+3\,\mathrm{SO_4^{2-}(aq)}+4\,\mathrm{H_2O(l)}$$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example $3.1.2$.

✓ Example 3.1.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$\mathrm{Al(s)}+\mathrm{H_2O(l)}\rightarrow\mathrm{[Al(OH)_4]^-(aq)}+\mathrm{H_2(g)}$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example $3.1.1$, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $\mathrm{[Al(OH)_4]^-}$. The oxidation state of hydrogen changes from +1 in $\mathrm{H_2O}$ to 0 in $\mathrm{H_2}$. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)}+\overset{+1}{H}_2O_{(aq)}\rightarrow[\overset{+3}{Al}(OH)_4]^-_{(aq)}+\overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.
    - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$

    - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
    - Reduction:

$$3\,\mathrm{H^+} + 3\,\mathrm{e^-} \longrightarrow 3\,\mathrm{H^0}\ (in\ \mathrm{H_2})$$

    - Oxidation:

$$\mathrm{Al^0} \longrightarrow \mathrm{Al^{3\,+}} + 3\,\mathrm{e^-}$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $\mathrm{H_2O}$ contains two protons, in this case, $3\,\mathrm{H^+}$ corresponds to $\frac{3}{2}\mathrm{H_2O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so $3\,\mathrm{H}$ corresponds to $\frac{3}{2}\mathrm{H_2}$.
    - Reduction:

$$\tfrac{3}{2}\mathrm{H_2O} + 3\,\mathrm{e^-} \longrightarrow \tfrac{3}{2}\mathrm{H_2}$$

    - Oxidation:

$$\mathrm{Al} \longrightarrow [\mathrm{Al(OH)_4}]^- + 3\,\mathrm{e^-}$$

6. Adding the equations and canceling the electrons gives

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2O} + \ 3\cancel{\mathrm{e^-}} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\mathrm{H_2} + \ 3\cancel{\mathrm{e^-}}$$
$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2O} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\mathrm{H_2}$$

To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,\mathrm{Al} + 3\,\mathrm{H_2O} \rightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two $\mathrm{OH^-}$ ions to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 3\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 6\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

9. Be sure the equation is balanced:
    1. Atoms:

$$2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H} \overset{\checkmark}{=} 2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H}$$

    2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,\mathrm{Al(s)} + 2\,\mathrm{OH^-(aq)} + 6\,\mathrm{H_2O(l)} \rightarrow 2\,[\mathrm{Al(OH)_4}]^-\mathrm{(aq)} + 3\,\mathrm{H_2(g)}$$

Thus 3 mol of H_2 gas are produced for every 2 mol of Al consumed.

? Exercise 3.1.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer

$$2\,MnO_4^-(aq) + 3\,NO_2^-(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,NO_3^-(aq) + 2\,OH^-(aq)$$

As suggested in Examples 3.1.1 and 3.1.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*

Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

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3.2: Voltaic (or Galvanic) Cells- Generating Electricity from Spontaneous Chemical Reactions

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:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

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 $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation $3.2.1$). 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 $3.2.1$). 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.

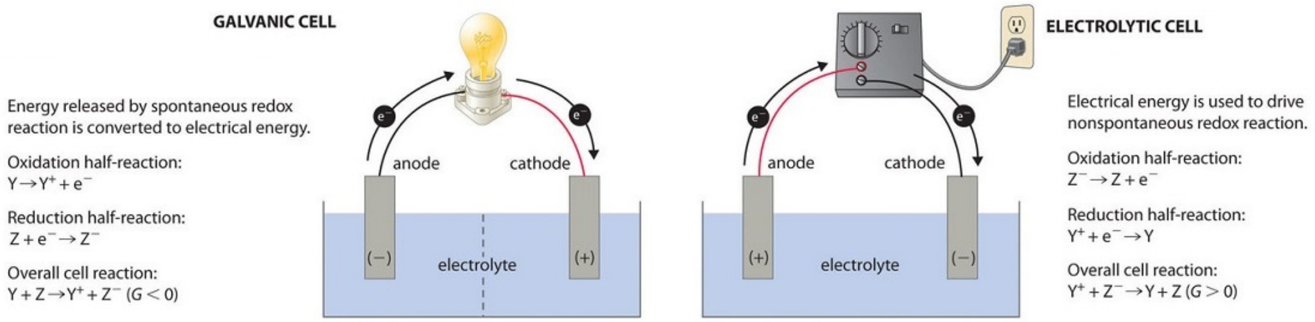

Figure $3.2.1$: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical 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:

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)} \tag{3.2.1}$$

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 $3.2.2$: 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 $\mathrm{Zn^{2+}(aq)}$ ions, while $\mathrm{Cu^{2+}(aq)}$ 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 $3.2.3a$. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ 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 $\mathrm{Na^+}$ or $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ or $\mathrm{SO_4^{2-}}$, 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 $\mathrm{Zn^{2+}}$ ions at the zinc electrode (the anode), and $\mathrm{Cu^{2+}}$ ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of $\mathrm{Zn^{2+}}$ ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of $\mathrm{Cu^{2+}}$ ions in the solution decreases (Figure $3.2.3b$). 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.

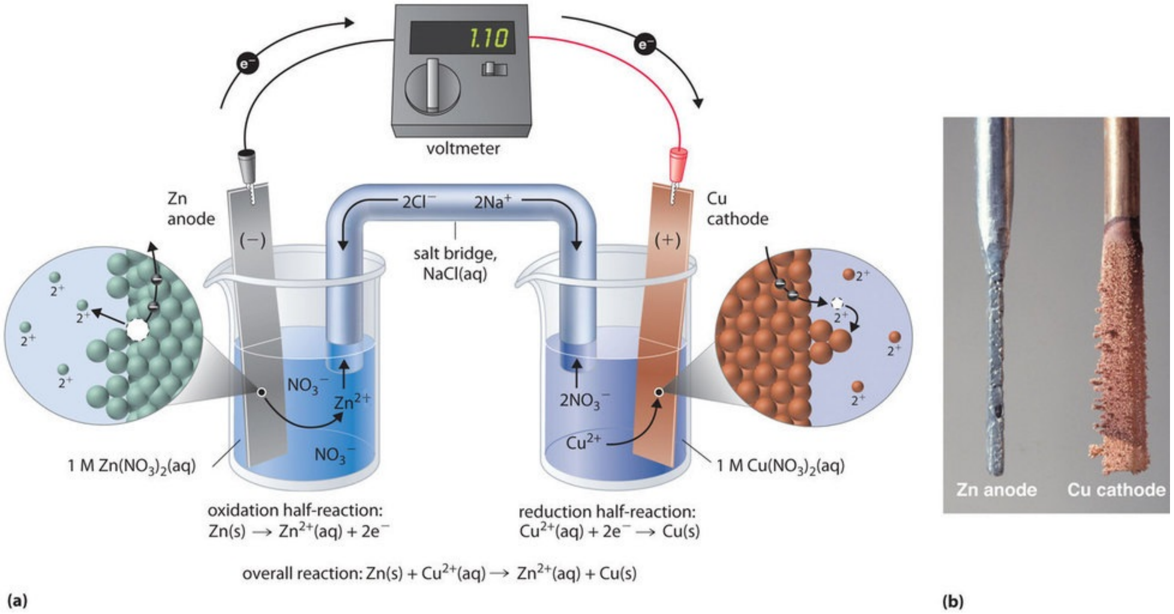

Figure $3.2.3$: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of $\mathrm{Cu^{2+}}$ ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of $\mathrm{Zn^{2+}}$ 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 $\mathrm{Zn^{2+}}$ ions in the left compartment, while $\mathrm{Cu^{2+}}$ 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 $\mathrm{Zn^{2+}(aq)}$ ions, while the Cu cathode gains mass as $\mathrm{Cu^{2+}(aq)}$ 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 $\mathrm{Zn^{2+}}$ solution would increase as the zinc metal dissolves, and the total positive charge in the $\mathrm{Cu^{2+}}$ solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the $\mathrm{Zn^{2+}}$ solution and a flow of cations into the $\mathrm{Cu^{2+}}$ 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 $3.2.3a$). 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 $3.2.1$.

> *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 3.2.1

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:

$$3\,\mathrm{Sn(s)} + 2\,\mathrm{NO_3^-(aq)} + 8\,\mathrm{H^+(aq)} \rightarrow 3\,\mathrm{Sn^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. 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:

A. 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.
B. 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:

$$\mathrm{NO_3^-(aq)} + 4\,\mathrm{H^+(aq)} + 3\,\mathrm{e^-} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}$$

oxidation:

$$\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$$

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 3.2.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ 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:

$$2\,\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Sn^{2+}(aq)} + 16\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Mn^{2+}(aq)} + 5\,\mathrm{Sn^{4+}(aq)} + 8\,\mathrm{H_2O(l)}$$

For this galvanic cell,

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

Answer a

$$\begin{aligned} \mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-} &\rightarrow \mathrm{Mn^{2+}(aq) + 4\,H_2O(l)} \\ \mathrm{Sn^{2+}(aq)} &\rightarrow \mathrm{Sn^{4+}(aq) + 2\,e^-} \end{aligned}$$

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 $\mathrm{Zn/Cu}$ cell shown in Figure $3.2.3a$ is written as follows:

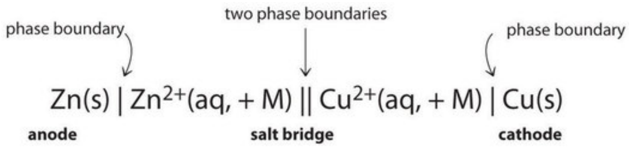

Figure $3.2.4$: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

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:

$$\mathrm{Pt(s)\,|\,H_2(g)|HCl(aq,\ 1\ M)\,|\,AgCl(s)\ Ag(s)}$$

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:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)}$$

anode reaction:

$$\mathrm{\tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

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 3.2.2

Draw a cell diagram for the galvanic cell described in Example 3.2.1. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

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 $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) 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 $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$$

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

? Exercise 3.2.2

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

$$\mathrm{Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)}$$

Answer

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

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.

3.2: Voltaic (or Galvanic) Cells- Generating Electricity from Spontaneous Chemical Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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3.3: Standard Reduction Potentials

Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

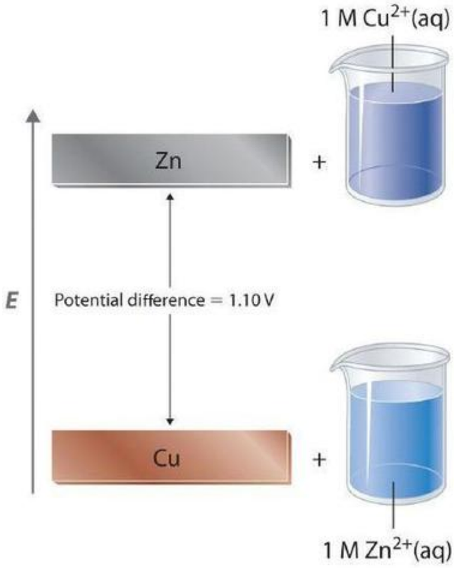

Figure 3.3.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 3.3.1 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E^\circ = 0.59\ V \tag{3.3.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} \tag{3.3.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 3.3.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

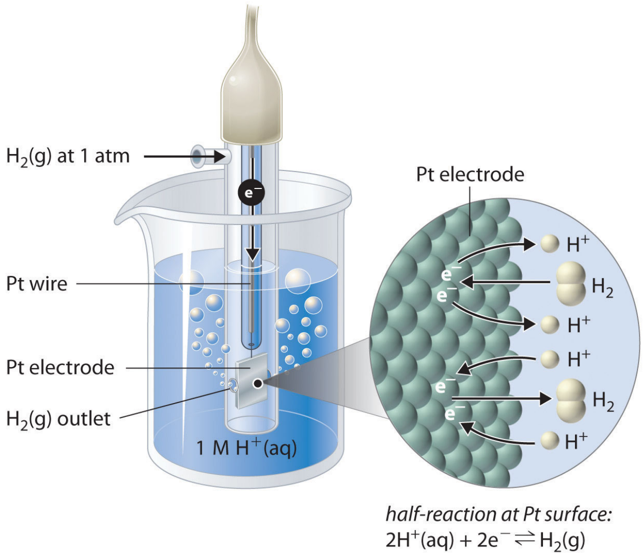

Figure 3.3.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 3.3.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{3.3.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

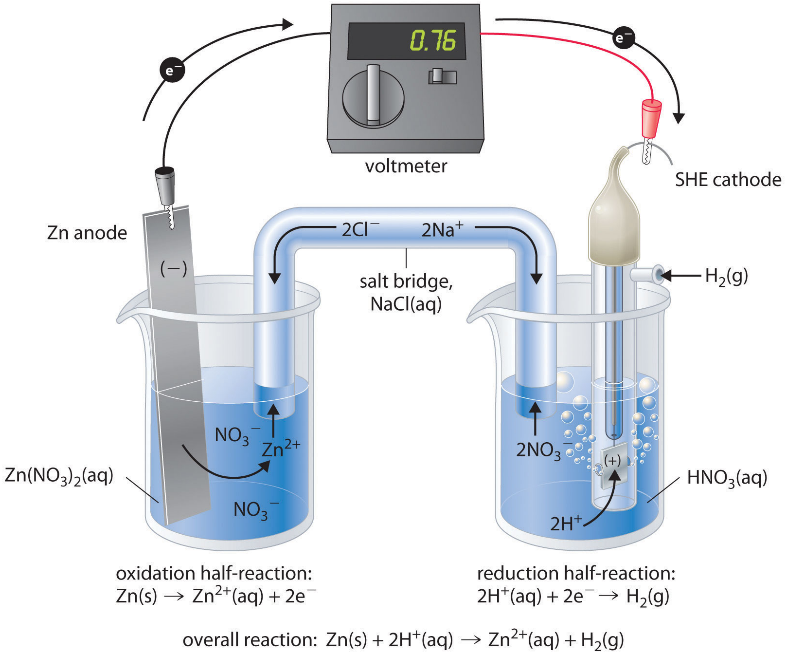

Figure 3.3.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E^\circ{}_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form Zn^{2+}(aq) ions while H^+(aq) ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure 3.3.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{3.3.4}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ{}_{cathode} = 0V \tag{3.3.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^\circ{}_{anode} = -0.76\ V \tag{3.3.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{3.3.7}$$

We then use Equation 3.3.2 to calculate the cell potential

$$\begin{aligned} E^\circ{}_{cell} &= E^\circ{}_{cathode} - E^\circ{}_{anode} \\ &= 0.76\ V \end{aligned}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for Zn^{2+}(aq) + $2e^-$ → Zn(s) is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E^\circ{}_{anode}$ from $E^\circ{}_{cathode}$ to obtain

$$E^\circ{}_{cell} : 0\ V - (-0.76\ V) = 0.76\ V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 3.3.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E^\circ{}_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E^\circ{}_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H$^+$ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{3.3.8}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E^\circ{}_{cathode} = 0.34\ V \tag{3.3.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E^\circ{}_{anode} = 0\ V \tag{3.3.10}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{3.3.11}$$

We then use Equation 3.3.2 to calculate the cell potential

$$\begin{aligned} E^\circ{}_{cell} &= E^\circ{}_{cathode} - E^\circ{}_{anode} \\ &= 0.34\ V \end{aligned}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Electrode Potentials and ECell: Electrode and Potentials and Ecell(opens in new window) [youtu.be]

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{3.3.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{3.3.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{3.3.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 3.3.13, two H^+ ions gain one electron each in the reduction; in Equation 3.3.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 3.3.13) by 3 and the oxidation half-reaction (Equation 3.3.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{3.3.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{3.3.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{3.3.17}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.18}$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{3.3.19}$$

The atoms also balance, so Equation 3.3.18 is a balanced chemical equation for the redox reaction depicted in Equation 3.3.12.

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 3.3.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{3.3.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{3.3.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{3.3.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{3.3.25}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{3.3.27}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 3.3.26 (the reductive half-reaction) by 3 and Equation 3.3.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{3.3.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{3.3.29}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.30}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.31}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 3.3.31 is identical to Equation 3.3.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 3.3.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 3.3.4):

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

- oxidation:

$$2\,I^-(aq) \longrightarrow I_2(aq) + 2\,e^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6\,\mathrm{I^-(aq)} \longrightarrow 3\,\mathrm{I_2(aq)} + 6\,\mathrm{e^-}$$

Adding the two half-reactions and canceling electrons,

$$\mathrm{Cr_2O_7^{2-}(aq)} + 14\,\mathrm{H^+(aq)} + 6\,\mathrm{I^-(aq)} \longrightarrow 2\,\mathrm{Cr^{3+}(aq)} + 7\,\mathrm{H_2O(l)} + 3\,\mathrm{I_2(aq)}$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$\begin{aligned}(-2) + 14 + (-6) &= +6 \\ +6 &\overset{\checkmark}{=} +6\end{aligned}$$

and atoms

$$2\,\mathrm{Cr} + 7\,\mathrm{O} + 14\,\mathrm{H} + 6\,\mathrm{I} \overset{\checkmark}{=} 2\,\mathrm{Cr} + 7\,\mathrm{O} + 14\,\mathrm{H} + 6\,\mathrm{I}$$

Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from $\mathrm{Cr^{6+}}$ in $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$, and $\mathrm{I^-}$ ions are oxidized to $\mathrm{I_2}$. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow Cr^{3+}_{(aq)}$$

- oxidation:

$$I^-_{(aq)} \rightarrow I_{2(aq)}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)}$$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^{-}(aq) \rightarrow 3I_2(s) + 6e^{-}$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\mathrm{Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 3\,I_2(aq)}$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 3.3.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid ($\mathrm{HNO_3}$), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$\mathrm{CuS(s) + HNO_3(aq) \rightarrow NO(g) + CuSO_4(aq)}$$

Balance this equation using the half-reaction method.

Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$\mathrm{3\,CuS(s) + 8\,HNO_3(aq) \longrightarrow 8\,NO(g) + 3\,CuSO_4(aq) + 4\,H_2O(l)}$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{3.3.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E^\circ{}_{cell}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^\circ{}_{cathode} = 0.34\ V \tag{3.3.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E^\circ{}_{anode} = -0.76\ V \tag{3.3.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{3.3.35}$$

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E^\circ{}_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E^\circ{}_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 3.3.2 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E^\circ{}_{cell}$ means that the reaction will occur spontaneously as written. A negative $E^\circ{}_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

✓ Example 3.3.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
B. Use Equation 3.3.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E^\circ_{anode} = -0.55$ V.

B Using the value given for $E^\circ{}_{cell}$ and the calculated value of E°_{anode}, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 3.3.2:

$$\begin{aligned} E^\circ{}_{cell} &= E^\circ{}_{cathode} - E^\circ{}_{anode} \\ 0.27\,V &= E^{o\,\circ}{}_{cathhode} - (-0.55\,V) \\ E^\circ_{cathode} &= -0.28\,V \end{aligned}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E^\circ_{cathode}$. Thus E° = −(−0.28 V) = 0.28 V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

? Exercise 3.3.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer

0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{3.3.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure $3.3.5$. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{3.3.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{3.3.38}$$

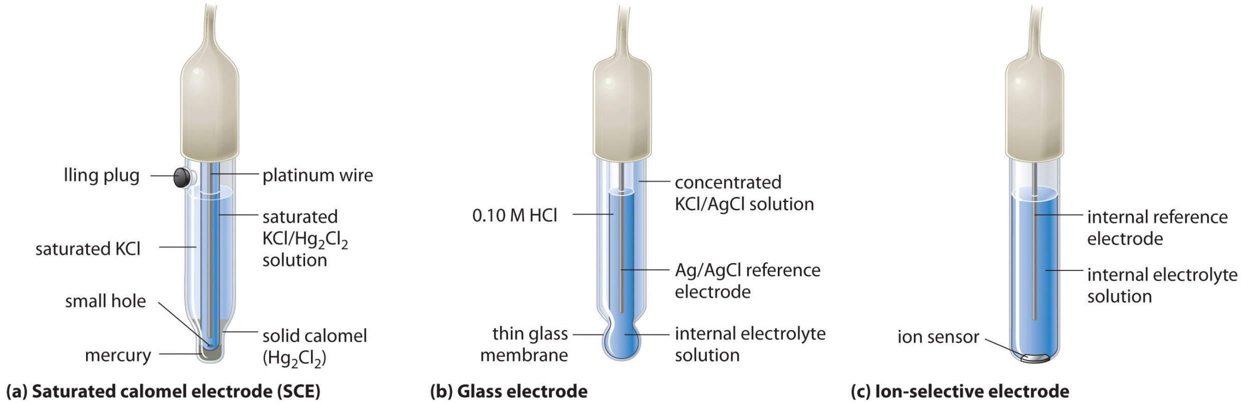

Figure 3.3.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 3.3.5. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that pH = −log$[H^+]$):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{3.3.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 3.3.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 3.3.1.

Table 3.3.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If E°_{cell} is positive, the reaction will occur spontaneously under standard conditions. If E°_{cell} is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

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3.4: Cell Potential, Gibbs Energy, and the Equilibrium Constant

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

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

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):

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

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):

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

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

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

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{3.4.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°$_{\text{cell}}$.

✓ Example 3.4.1

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^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Then use Equation 3.4.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} & E^\circ_{\text{anode}} = 1.09\text{ V} \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^o is not affected:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^\circ_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} & E^\circ_{\text{anode}} = 1.09\text{ V} \\ \hline \text{overall:} & \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} & E^\circ_{\text{cell}} = 0.27\text{ V} \end{array}$$

B

We can now calculate ΔG° using Equation 3.4.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^\circ &= -(n)(F)(E^\circ_{\text{cell}}) \\ &= -(6\text{ mole})[96,485\text{ J}/(\text{V}\cdot\text{mol})(0.27\text{ V})] \\ &= -15.6\ \times 10^4\text{ J} \\ &= -156\text{ kJ}/\text{mol }\mathrm{Cr_2O_7^{2-}} \end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

? Exercise 3.4.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$\mathrm{2\,Fe^{3\,+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2\,+}(aq) + I_2(s)}$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; 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 $\mathrm{Fe^{3+}(aq)}$ to $\mathrm{Fe(s)}$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)} \quad E^\circ = +0.77V$$

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ = -0.45V$$

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^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

$$\begin{aligned}
\mathrm{Fe^{3+}(aq) + e^-} &\rightarrow \mathrm{Fe^{2+}(aq)} & \Delta G^\circ &= -(1)(F)(0.77\text{ V}) \\
\mathrm{Fe^{2+}(aq) + 2\,e^-} &\rightarrow \mathrm{Fe(s)} & \Delta G^\circ &= -(2)(F)(-0.45\text{ V}) \\
\mathrm{Fe^{3+}(aq) + 3\,e^-} &\rightarrow \mathrm{Fe(s)} & \Delta G^\circ &= [-(1)(F)(0.77\text{ V})] + [-(2)(F)(-0.45\text{ V})]
\end{aligned}$$

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

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

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 3.4.1 and solving for E^o gives the following:

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

This value of E^o 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^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ 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 3.4.1), we can write

$$-nFE^\circ_{cell} = -RT\ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{3.4.2}$$

For $T = 298\ K$, Equation 3.4.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J}/(\text{mol}\cdot\text{K})(298\ \text{K})]}{n[96,485\ \text{J}/(\text{V}\cdot\text{mol})]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{3.4.3}$$

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 3.4.2

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:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 3.4.3 to solve for $\log K$ and then K.

Solution

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

cathode:	$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 3.4.3 for log K and inserting the values of n and E^o,

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

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 3.4.2

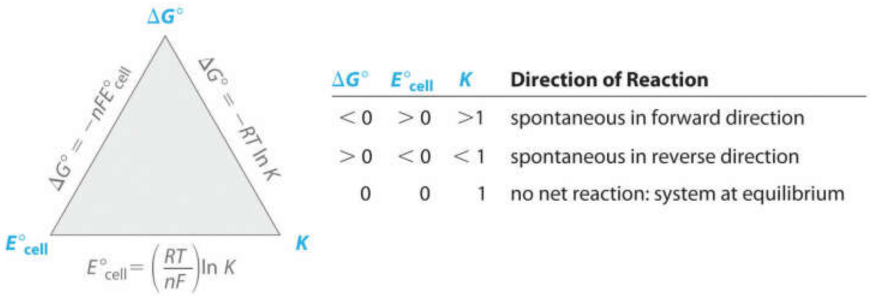
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}(\text{aq})$ with oxygen to produce $\text{Sn}^{4+}(\text{aq})$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,\text{Sn}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\,\text{H}^+(\text{aq}) \rightleftharpoons 2\,\text{Sn}^{4+}(\text{aq}) + 2\,\text{H}_2\text{O}(\text{l})$$

Answer

5.7×10^{72}

Figure 3.4.1 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 ($\Delta G° < 0$). 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.



$\Delta G°$	$E°_{cell}$	K	**Direction of Reaction**
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 3.4.1: 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, $\Delta G°$, 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 $\Delta G°$ 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^o 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^o 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°.

3.4: Cell Potential, Gibbs Energy, and the Equilibrium Constant is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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3.5: Cell Potential and Concentration

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:

$$\Delta G = \Delta G^\circ + RT\ln Q \tag{3.5.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 3.5.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT\ln Q \tag{3.5.2}$$

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

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{RT}{nF}\right)\ln Q \tag{3.5.3}$$

Equation 3.5.3 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 3.5.3 reduces to Equation 3.5.4 and 3.5.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{RT}{nF}\right)\ln K = 0 \tag{3.5.4}$$

since

$$E^\circ_\text{cell} = \left(\dfrac{RT}{nF}\right)\ln K \tag{3.5.5}$$

Substituting the values of the constants into Equation 3.5.3 with $T = 298\ K$ 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):

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{0.0591\text{ V}}{n}\right)\log Q \tag{3.5.6}$$

The Power of the Nernst Equation

The Nernst Equation (3.5.3) 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 3.5.6 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 3.5.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 3.5.1

The following reaction proceeds spontaneously under standard conditions because E°$_{cell}$ > 0 (which means that ΔG° < 0):

$$2\,Ce^{4+}(aq) + 2\,Cl^{-}(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g) \qquad E^{\circ}_{cell} = 0.25\,V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: [Ce^{4+}] = 0.013 M, [Ce^{3+}] = 0.60 M, [Cl^{-}] = 0.0030 M, P_{Cl_2} = 1.0 atm, and T = 25°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 3.5.6 instead of Equation 3.5.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^{-} \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl$_2$, and the value of E°$_{cell}$ into Equation 3.5.6,

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

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 3.5.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^{-}(aq) \longrightarrow 4\,MnO_4^{-}(aq) + 2\,H_2O(l) \quad E^{\circ}{}_{cell} = -0.20\,V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, [MNO$_4^{-}$] = 1.0 × 10^{-4} M, and T = 25°C.

Answer

E$_{cell}$ = −0.22 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:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^{\circ}cell = 1.10V \tag{3.5.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 3.5.6:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{3.5.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{3.5.9}$$

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 $E_{\text{cell}} = E°_{\text{cell}}$. 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 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

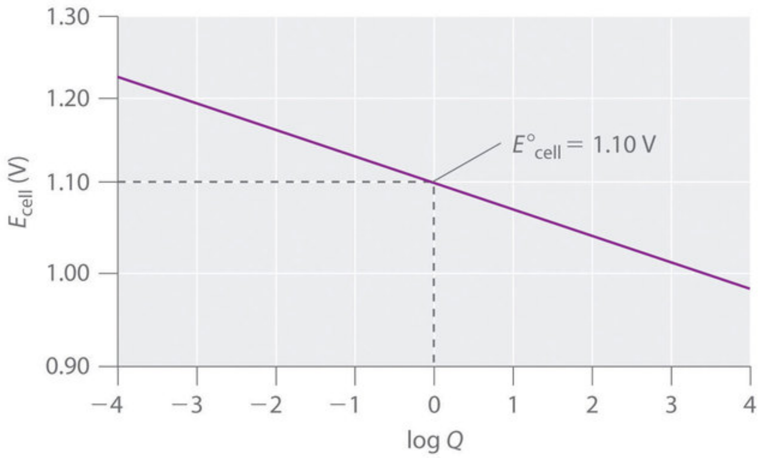

Figure 3.5.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{\text{cell}}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$, log Q = 0 and $E_{\text{cell}} = E°_{\text{cell}} = 1.10$ 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 3.5.1. 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:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q = 0 \tag{3.5.10}$$

$$E^{\circ} = \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{3.5.11}$$

$$\log Q = \frac{E^{\circ} n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{3.5.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{3.5.13}$$

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:

$$\mathrm{Ag(s)} \,|\, \mathrm{Ag^+}(aq, 0.010\ M) \,||\, \mathrm{Ag^+}(aq, 1.0\ M) \,|\, \mathrm{Ag(s)} \tag{3.5.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag(s)} \tag{3.5.15}$$

anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{3.5.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{3.5.17}$$

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 $E°_{cathode} = -E°_{anode}$:

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

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 ($E_{cell} = 0$).

✓ Example 3.5.2

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°C).

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

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. 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:

$$\mathrm{Mn}^{2+}(aq, 2.0\,M) \rightarrow \mathrm{Mn}^{2+}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 3.5.6:

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

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 3.5.2

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_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)}$$

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.

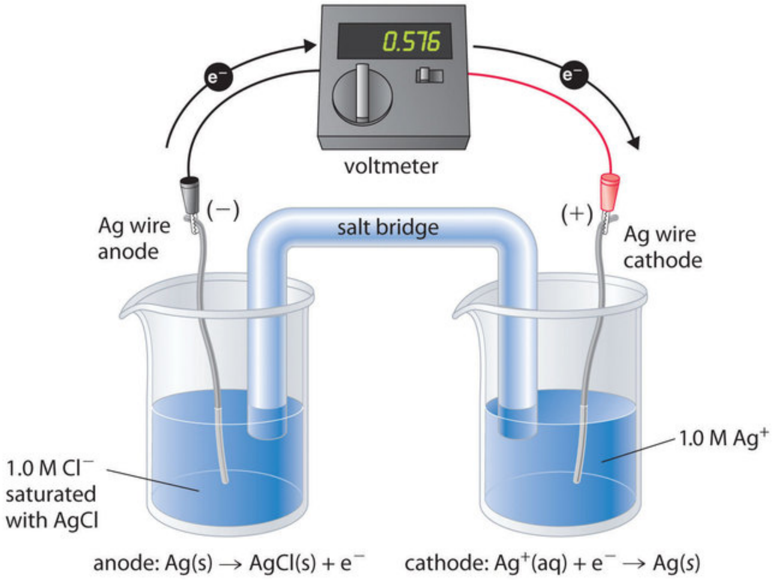

Figure 3.5.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ 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 3.5.1, which is designed to measure the solubility product of silver chloride:

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

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 $[Cl^-]$ and substituting:

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

The overall cell reaction is as follows:

$$\mathrm{Ag^+(aq, concentrated)} \rightarrow \mathrm{Ag^+(aq, dilute)}$$

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

$$\begin{aligned}E_{\text{cell}} &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{1}\right)\log\left(\frac{[\mathrm{Ag^+}]_{\text{dilute}}}{[\mathrm{Ag^+}]_{\text{concentrated}}}\right) \\ &= -0.0591\text{ V }\log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\text{ V }\log K_{\text{sp}}\end{aligned} \tag{3.5.18}$$

By closing the circuit, we can measure the potential caused by the difference in [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 3.5.18 for K_{sp},

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

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 3.5.3: 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 3.5.1, 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:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.
B. 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}:

$$\begin{aligned}[\mathrm{Pb^{2+}}][\mathrm{SO_4^{2-}}] &= K_{\mathrm{sp}} \\ [\mathrm{Pb^{2+}}] &= \frac{K_{\mathrm{sp}}}{[\mathrm{SO_4^{2-}}]} = \frac{K_{\mathrm{sp}}}{1.0\ \mathrm{M}} = K_{\mathrm{sp}}\end{aligned}$$

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

$$\mathrm{Pb^{2+}(aq,\ concentrated) \rightarrow Pb^{2+}(aq,\ dilute)}$$

so

$$\begin{aligned}E_{\mathrm{cell}} &= E^{\circ}_{\mathrm{cell}} - \left(\frac{0.0591}{n}\right)\log Q \\ 0.230\ \mathrm{V} &= 0\ \mathrm{V} - \left(\frac{0.0591\ \mathrm{V}}{2}\right)\log\left(\frac{[\mathrm{Pb^{2+}}]_{\mathrm{dilute}}}{[\mathrm{Pb^{2+}}]_{\mathrm{concentrated}}}\right) = -0.0296\ \mathrm{V}\log\left(\frac{K_{\mathrm{sp}}}{1.0}\right) \\ -7.77 &= \log K_{\mathrm{sp}} \\ 1.7\times10^{-8} &= K_{\mathrm{sp}}\end{aligned}$$

? Exercise 3.5.3

A concentration cell similar to the one described in Example 3.5.3 contains a 1.0 M solution of lanthanum nitrate $[La(NO_3)_3]$ 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

5.7×10^{-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 3.5.3, 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 $[H^+]$ using a pH meter, as illustrated below.

✓ Example 3.5.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} 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:

$$\mathrm{Zn(s)|Zn^{2+}}(aq, 1.0\,M)||\mathrm{H^+}(aq, ?\,M)|\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

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:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for −log[H$^+$] to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$\mathrm{Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)} \quad E° = 0.76\ \mathrm{V}$$

B By substituting the given values into the simplified Nernst equation (Equation 3.5.6), we can calculate [H$^+$] under nonstandard conditions:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\left(\frac{[\mathrm{Zn^{2+}}]P_{\mathrm{H_2}}}{[\mathrm{H^+}]^2}\right) \\ 0.26\ \text{V} &= 0.76\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\mathrm{H^+}]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[\mathrm{H^+}]^2}\right) = \log[\mathrm{H^+}]^{-2} = (-2)\log[\mathrm{H^+}] \\ 8.46 &= -\log[\mathrm{H^+}] \\ 8.5 &= \text{pH} \end{aligned}$$

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

? Exercise 3.5.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{\text{cathode}}$ = 1.23 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:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} 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 ΔG = 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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CHAPTER OVERVIEW

4: Current

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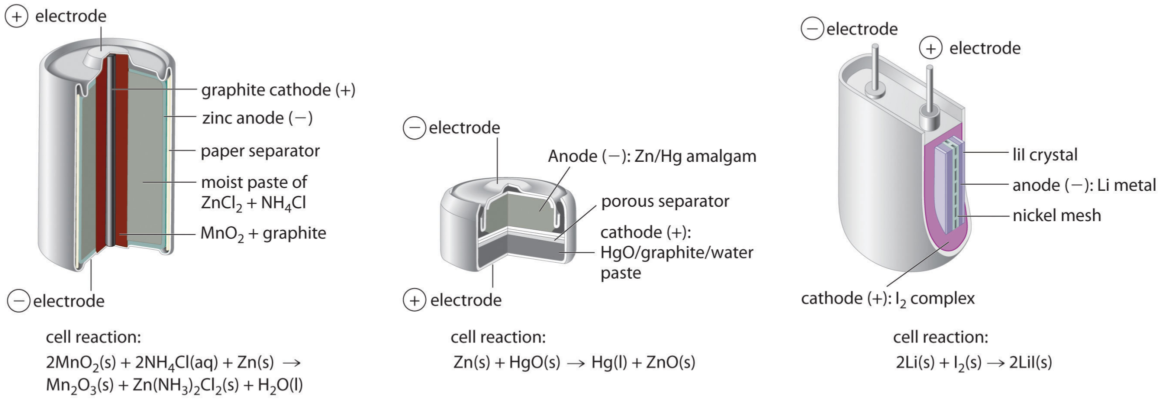
4.1: Batteries- Using Chemistry to Generate Electricity

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 4.1.1). 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.



(a) Leclanché dry cell **(b) Button battery** **(c) Lithium-iodine battery**

Figure 4.1.1: 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 4.1.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$$

- anode (oxidation):

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

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:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{4.1.1}$$

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.

Close up of a hand holding one double <span class=
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)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

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 $4.1.1b$).

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):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$

  with $E_{cell} = 1.35\,V$.
- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$$

- anode (silver battery):

$$\mathrm{Zn} + 2\,\mathrm{OH}^- \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\,\mathrm{e}^-$$

- Overall reaction (silver battery):

$$\mathrm{Zn(s)} + 2\,\mathrm{Ag_2O(s)} \longrightarrow 2\,\mathrm{Ag(s)} + \mathrm{ZnO(s)}$$

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

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):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{4.1.2}$$

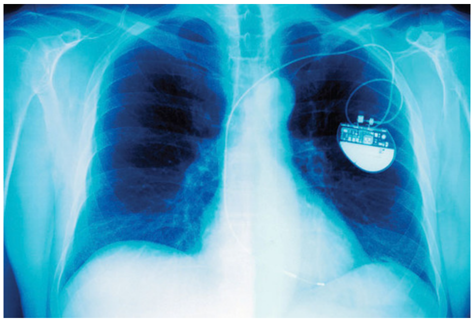
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{4.1.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{4.1.4}$$

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



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 $4.1.1$, 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 $4.1.2$, 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.

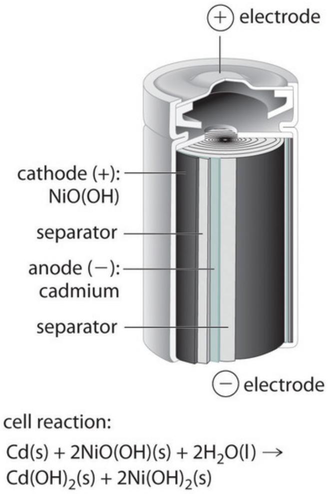


Figure 4.1.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

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

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{4.1.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{4.1.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{4.1.7}$$

$$E_{cell} = 1.4V$$

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:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

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.

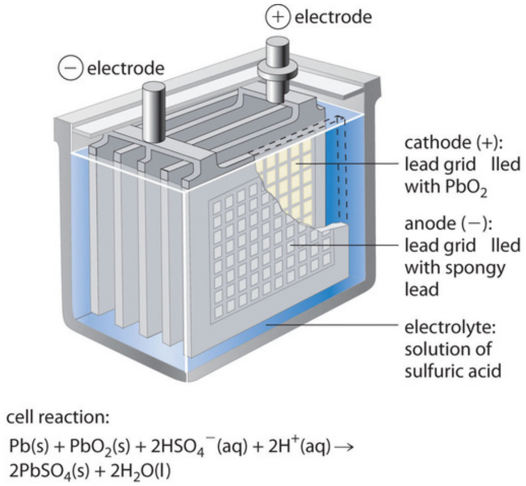


Figure 4.1.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value 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 4.1.3, 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):

\[PbO_{2(s)} + HSO^−_{4(aq)} + 3H^+_{(aq)} + 2e^− \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{4.1.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{4.1.9}$$

and $E^\circ_{cell} = 2.041\ V$

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:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{4.1.10}$$

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.

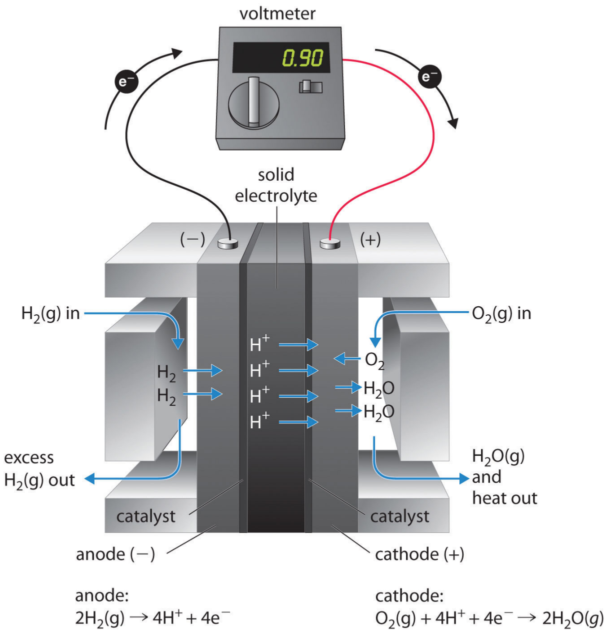


Figure 4.1.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte 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 4.1.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{4.1.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{4.1.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{4.1.13}$$

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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4.2: Electrolysis- Driving Non-spontaneous Chemical Reactions with Electricity

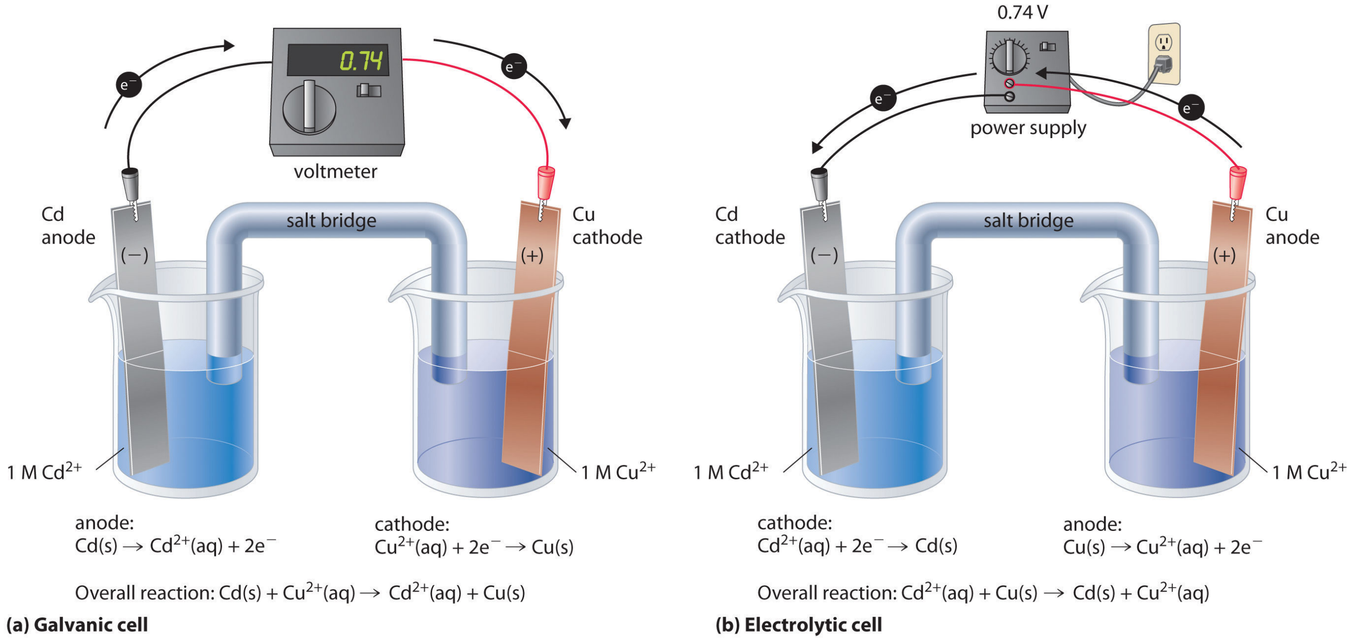
Learning Objectives

- 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 $4.2.1a$).



(a) Galvanic cell **(b) Electrolytic cell**

Figure 4.2.1: 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 $Cd^{2+}(aq)$ and a Cu electrode immersed in 1 M $Cu^{2+}(aq)$ are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to $Cd^{2+}(aq)$ at the anode, and $Cu^{2+}(aq)$ 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 $Cu^{2+}(aq)$] and into the Cd electrode [which is now the cathode, at which $Cd^{2+}(aq)$ 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:

$$\mathrm{Cd(s) + Cu^{2\,+}(aq) \rightarrow Cd^{2\,+}(aq) + Cu(s)}$$

with $E^\circ{}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^o < 0$):

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_\mathrm{cell} \\ &= -(\mathrm{2\ mol\ e^-})[\mathrm{96{,}485\ J/(V\cdot mol)}](\mathrm{0.74\ V}) \\ &= -\mathrm{140\ kJ\ (per\ mole\ Cd)} \end{aligned}$$

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 $4.2.1b$). 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:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{4.2.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{4.2.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{4.2.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, 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 $4.2.1$.

Table $4.2.1$: 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:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{4.2.4}$$

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 $4.2.2$). 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.

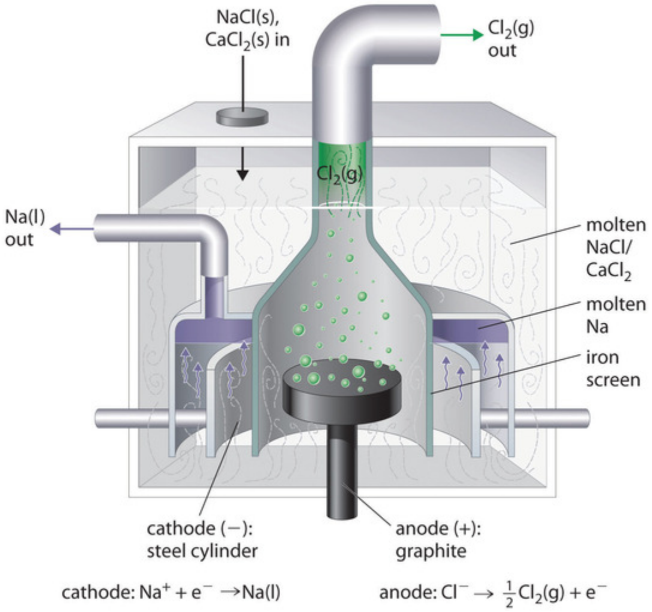


Figure 4.2.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium 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 (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,\mathrm{Al_2O_3(l)} + 3\,\mathrm{C(s)} \longrightarrow 4\,\mathrm{Al(l)} + 3\,\mathrm{CO_2(g)} \tag{4.2.5}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(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 $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 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 4.2.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. 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.
B. 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 (χ = 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 4.2.1

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 4.2.3).

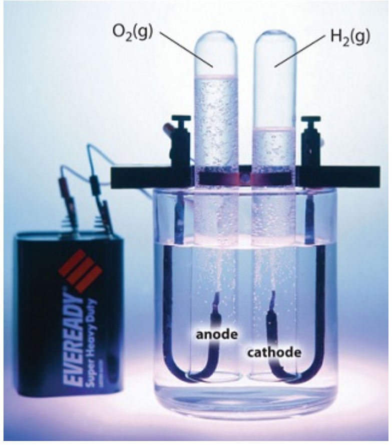


Figure 4.2.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{4.2.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{4.2.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{4.2.8}$$

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 $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{4.2.9}$$

$$= -1.23\text{ V} - \left(\frac{0.0591\text{ V}}{4}\right)\log(1) = -1.23\text{ V} \tag{4.2.10}$$

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 pH 7.0.

In practice, a voltage about 0.4–0.6 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 4.2.4.

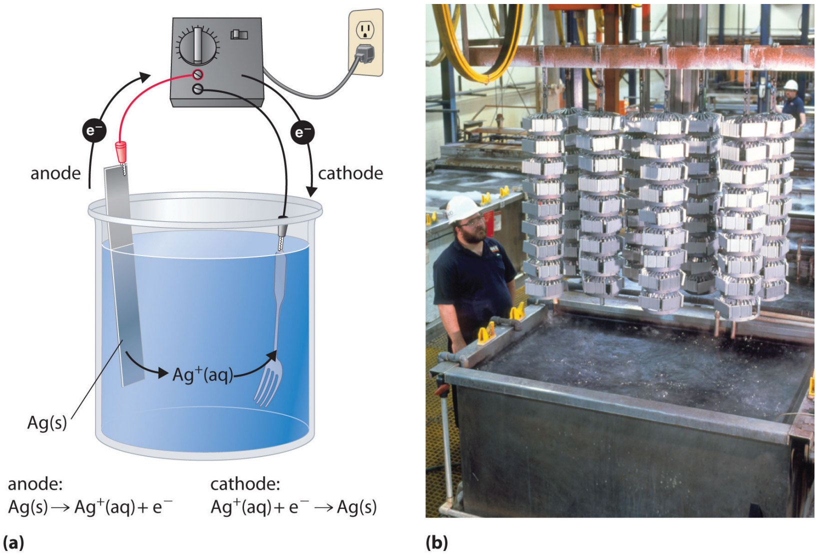


Figure 4.2.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually 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):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ{}_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E^\circ{}_{anode} = 0.80V$$

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 $E^o_{cell} = 0\,V$, 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

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

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2+}}$ 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):

$$q = I \times t \tag{4.2.11}$$

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 $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\ \mathrm{A})(6.0\ \mathrm{min})(60\ \mathrm{s/min}) \\ &= 220\ \mathrm{A \cdot s} \\ &= 220\ \mathrm{C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2+}}$ is therefore

$$\begin{aligned} \mathrm{moles\ e^-} &= \frac{220\ \mathrm{C}}{96{,}485\ \mathrm{C/mol}} \\ &= 2.3 \times 10^{-3}\ \mathrm{mol\ e^-} \end{aligned}$$

Because two electrons are required to reduce a single $\mathrm{Cu^{2+}}$ ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} 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 4.2.2

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:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. 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 $Ag^+(aq) + e^- \rightarrow Ag(s)$, 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 4.2.2

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 Al_2O_3/Na_3AlF_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 H_2 and O_2 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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