CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Unit Overview

Every portable electronic device is fueled by chemistry, specifically through oxidation-reduction or "redox" reactions. In redox reactions, one compound gains electrons (reduction) and one compound loses them (oxidation). Chemists can set up reactions so that electrons are forced to move in a certain way to create an electrical current. Metals often play a key role in redox reactions, which are essential to all aspects of chemistry, particularly in many biochemical processes.

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Sections

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Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 1: Introduction

We're out running an errand when the phone rings. One of our friends has an extra ticket to this weekend's game, and would love to take us. After we get off the phone, we realize that the battery is running low, so we make sure to plug it into the charger when we return home. The weather is nice, so we take a laptop outside to work on the paper due on Monday.

Batteries, especially rechargeable ones, have made communication much more efficient and computing more portable in the past two decades. Improvement in battery technology has allowed for a scaling down of sizes, with more power and longer life in progressively smaller packaging. Every portable electronic device, whether we realize it or not, is fueled by chemistry—specifically, the chemistry of **oxidation** and **reduction**, or **redox**. (Figure 11-1)

Figure 11-1. Rechargeable Batteries

Many personal electronics use a rechargeable battery system for power. The batteries run on oxidation-reduction, or redox, chemistry.

In Unit 4, we learned about oxidation states, and in Unit 10 we saw simple examples of reactions in which those oxidation states change. When the oxidation states or reactants change, one species loses electrons (referred to as "oxidation" of the species) and another gains the electrons (referred to as "reduction"). When a redox reaction can be set up so that the electrons are forced to move through a wire, it is producing electricity, or electrical current. This makes electrochemistry (the name given to various applications of redox reactions) an incredibly useful branch of chemistry.

We may also recall from Unit 9 that not all reactions proceed without outside intervention. Application of an electric current can force redox reactions to run "backwards," that is, in the nonspontaneous direction. This, too, can be used to great advantage. For example, recharging a phone forces a redox reaction backwards, so that it can go right back to running in the forward direction and allow us to take that call from our friend. In this unit, we will take a closer look at how redox processes work, in both directions.

We also will examine transition metal chemistry. Many redox reactions involve transition metals, and the presence of these metals is often the reason for special disposal instructions for electronic equipment. Metals can do plenty of interesting things besides redox though. Many of them can produce intensely colored compounds, a phenomenon which is significantly less common in compounds made entirely of nonmetals. Several metals also play critical roles in physiological processes, even when they are present only in trace amounts. We will see a few of these examples in the final sections of this unit.

Glossary

Oxidation
Loss of electrons by one species over the course of a chemical reaction.

Redox
The shorthand term for a "reduction-oxidation" reaction.

Reduction
A reaction in which an atom, molecule, or ion gains electrons. Reduction is always accompanied by a separate oxidation process, a reaction in which another reactant loses the electrons.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 2: The Activity Series

As we saw in Units 4 and 10, many metals can react with acids (and some even with water!), and several nonmetals can react with aqueous solutions of salts, in reactions referred to as "single displacement." In these reactions, one reactant is an element and one product is a different element. The reaction of magnesium metal with aqueous hydrochloric acid:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

as well as the reaction of sodium with water:

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Both release hydrogen gas when the metal reacts. Similarly, the reaction of chlorine with sodium bromide generates elemental bromine:

$$Cl_{2(aq)} + 2\ NaBr_{(aq)} \rightarrow 2NaCl_{(aq)} + Br_{2(l)}$$

In all of these processes, whichever reactant is in its elemental form is converted to its most stable ionic form to substitute for either the cation or the anion of the compound on the reactant side. As we may recall from our introduction to ionic compounds, ions carry specific charges (their oxidation states) and elements by themselves do not. An uncharged element is said to have an oxidation state of zero. If an element reacts to become part of a compound, its oxidation state has to change; similarly, if a compound has one of its components displaced into its elemental form, the oxidation state of the element changes. Displacement reactions are, therefore, the simplest examples of redox processes. A redox process must involve both an oxidation and a reduction; the electrons must be transferred from one of the reactants to another one. Anything in its elemental form has an oxidation number of zero, but the identification of the oxidation and reduction processes requires a comparison between the initial and final oxidation states of each element.

Figure 11-2. The Activity Series for Metals

In this list, metals are arranged according to their ability to lose electrons (be oxidized). The more easily a metal is oxidized, the more reactive it tends to be. Indeed, the metals at the top of the list are highly reactive, while the metals at the bottom are known and used for their lack of reactivity.

Magnesium metal reacts readily with aqueous acid, displacing the hydrogen from the acid and reducing it to hydrogen gas. Sodium metal can even displace hydrogen from water! Both of these reactions are vigorous, generating plenty of bubbles, heat, and even sparks. But what if we dropped copper metal, or gold, into a solution of acid? Even in concentrated solutions of strong acids, very little bubbling occurs, and certainly no sparks. Similarly, zinc metal reacts readily with copper sulfate solution, producing a precipitate and diminishing the intensity of the copper solution's characteristic blue color; but copper metal in a solution of zinc sulfate produces no apparent reaction. For all of these processes, the equation for the expected reaction can be written and balanced, but the reaction does not always occur. The fact that the reactions do not all occur is the basis for the **activity series**. (Figure 11-2)

The activity series appears, at first, to be a simple list of metals. Hydrogen is included on the list. The order, however, is critical. The series itself was developed based on observations of several different reactions, but the results can be used to predict, not just explain, the results of a reaction. The activity series is organized by reactivity, such that an element on the list will be able to displace ions of any element below it. The higher on the list, the more reactive an element is. Because the activity series is usually written only in terms of metals and hydrogen, "reactivity" in this case is specifically oxidation. Whichever element is displaced in the reaction gets reduced.

The prediction of whether or not a displacement reaction will proceed as written is as simple as finding the two metals involved on the activity series: If the metal in its elemental form on the reactant side is higher up on the activity series, the reaction will proceed as written. Similarly, the activity series can be viewed as a gauge of relative stabilities of metals or ions: The less reactive an element is, the more stable it is; the more reactive an element is, the more stable its ion must be.

As useful as the activity series is, however, it does not explain or predict the outcome of every possible redox reaction. For example, the displacement of halide ions by halogens is not accounted for, since the halogens do not appear on the list. In order to describe and predict these reactions, we need a more comprehensive list than the activity series. As we will see, the more comprehensive list provides not only a qualitative view of reactivity, but a quantitative one as well. From this, we can begin to apply redox processes and do useful things with them.

Glossary

Activity series

A list of various chemical species arranged in order of reactivity. It is usually used to describe the ability of various metals to displace hydrogen from water or from acids.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 3: Half-Reactions—Build a Redox Reaction

One of the critical reasons why redox reactions are so important and useful is that they ultimately can be used to produce energy. In order to determine how much energy can be produced, however, we must have a convenient way to analyze redox reactions quantitatively. Further, in order to develop or improve useful applications of redox processes, we must have a convenient way to analyze possible variations of the reactants. This quantitative analysis is made simpler by examining the oxidation and the reduction separately.

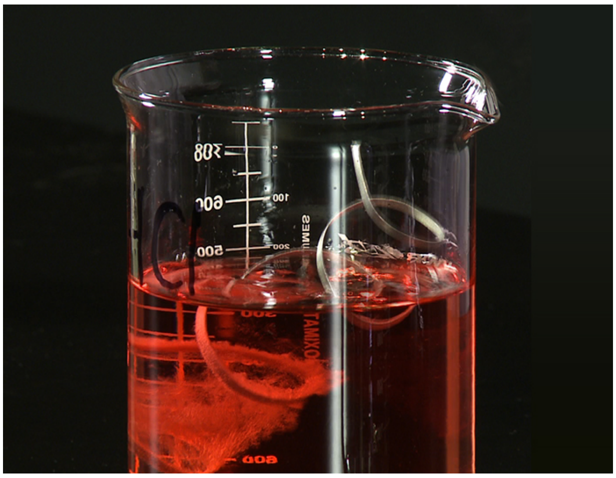

Figure 11-3. Oxidation of Magnesium

A demonstration of magnesium getting oxidized in a solution of hydrochloric acid and producing hydrogen bubbles.

In a redox reaction, the oxidation states of reacting species change as electrons are transferred from one species to another. Just as the elements in a chemical reaction must all be accounted for on both sides of the equation, all the electrons must be accounted for. But if we examine the oxidation states in the reaction of magnesium with aqueous acid (Figure 11-3), as shown in Section 2 of this unit, we see that each magnesium atom loses two electrons, but each hydrogen gains only one:

$$Mg^{(0)}{}_{(s)} + 2H^{+}{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + H_2^{(0)}{}_{(g)}$$

In this case, the balanced equation already accounts for the discrepancy; two hydrogen ions combine to form hydrogen gas, and so each takes one of the two electrons that a magnesium atom gives up. The balanced equation does not include the electrons explicitly; the redox can be understood merely by counting the oxidation states of the reactants and products. Not all redox processes are so straightforward, however, so the analysis of redox processes is typically based on **half-reactions**. In a half-reaction, either the oxidation or the reduction is described, with the electrons explicitly included as products (for oxidation) or reactants (for reduction).

If we divide the reaction above into half-reactions, we have the oxidation:

$$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$$

and the reduction:

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

Note that the chloride ions are spectator ions, because neither their oxidation state nor their physical state changes during the reaction. Each half-reaction involves the same number of electrons; so the combination of the two reactions, canceling out anything that appears on both sides, yields the net ionic equation for the full reaction.

Permanganate Ion: An Excellent Oxidizing Agent

We will see in the latter portion of this unit that compounds containing transition metals exhibit not only some very interesting chemistry, but also some very vivid colors. One of the many examples of both of these is the permanganate ion, MnO_4^-. Permanganate is an excellent oxidizing agent; that is, it is very good at taking electrons away form other chemical species. Its redox behavior alone would make it a useful reagent, but it also is an intense shade of purple—a color which disappears as the redox reaction proceeds. This makes the ion a built-in indicator when it is used in redox titrations, as well as a great characterization test for a variety of organic molecules.

Potassium permanganate can oxidize many chemical compounds, which in turn reduces the manganese from its +7 oxidation state to a lower oxidation state. When this happens, the deep purple color disappears—a very noticeable indicator that a reaction has taken place. © Wikimedia Commons, Public Domain.

In the permanganate ion, the manganese has an oxidation state of +7. Depending on the reaction, the manganese often adopts an oxidation state of +4 or +2. This can complicate the balancing of the equation if the other half-reaction generates an even number of electrons. For reactions of permanganate, as with any more complicated redox processes, analysis of the individual half-reactions can simplify the analysis of the reaction overall. If we consider the reaction of permanganate ions with SO_2 in the following unbalanced reaction:

$MnO_4^- + SO_2 \rightarrow SO_4^{2-} + Mn^{2+}$

we have the following half-reactions:

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ (oxidation)

$MNO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (reduction)

Because the numbers of electrons lost and gained are not equal, the equation is still unbalanced. To reconcile the difference, each half-reaction is multiplied by a coefficient to give the lowest common multiple of the two numbers of electrons. The oxidation half is multiplied by 5 and the reduction half is multiplied by 2, to yield the following:

$5SO_2 + 10H_2O \rightarrow 5SO_4^{2-} + 20H^+ + 10e^-$ (oxidation)

$2MNO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$ (reduction)

These half-reactions now involve equal numbers of electrons, and so they can be added together to give:

$5SO_2 + 2H_2O + 2MNO_4^- \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

Remember: The half-reactions make this analysis easier, but they don't happen independently of one another. In order for a species to lose electrons, those electrons must all have a place to go.

While this appears to be mostly a bookkeeping method in terms of balancing equations, balanced half-reactions are the basis of both the activity series and, as we will see in the next section, the table of standard reduction potentials. Recall that in the activity series, metals are listed according to the relative ease with which they lose electrons; therefore, a comparison between the reactivities of any two metals on the list is the proverbial apple-to-apple method. This allows for great flexibility; and, as we will see, the table of standard reduction potentials allows for even more flexibility. In a reaction, however, the more active metal displaces the less active metal from a compound, and so the less active metal ultimately gains the electrons lost by the more active one. The oxidation and reduction must happen in tandem in order for the reaction to occur, even though all the species in the reaction appear in the chart in terms of their oxidation behavior. Since any metal can displace from a compound any metal appearing below it on the activity series, any pairing of metals on the list can be expressed in terms of how the reaction will proceed. One of the two half-reactions therefore must be written in the opposite direction as it appears on the chart in order to write a balanced equation for the process. The overall equation is not balanced unless the electrons cancel from both half-reactions, and so each half-reaction is multiplied by whatever coefficient will yield the common multiple.

Glossary

Half-reaction

A chemical reaction balanced with electrons to show only the reduction half or the oxidation half of an electrochemical reaction.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 4: Electrons into Energy

As we saw in the activity series, patterns of reactivity can be tabulated. In the activity series, the patterns of reactivity are tabulated in terms of oxidation of metals. For the more general view of redox processes, this tabulation is made in the table of **standard reduction potential**, designated *E*°. As the name implies, half-reactions are all written as reductions, and the reactions are listed according to how favorable that reduction process is. As with the activity series, the reduction half-reactions are ordered according to observed patterns of reactivity, with everything expressed in terms of reduction. A quick comparison between any two half-reactions is as simple as looking at the order on the table. The table of reduction potentials has an advantage over the activity series by including numerical values, which allows for a quantitative, not just qualitative, view. The values assigned to reduction half-reactions are normalized against a common reference point: the Standard Hydrogen Electrode, or SHE. The reduction potential for this half-reaction (the reduction of hydrogen ions to form hydrogen gas) is defined as 0.00V, and all other half-reactions are measured against this value. (Figure 11-4)

Standard Potential (V)	Reduction Half-Reaction
1.51	$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$
1.33	$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$
1.23	$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$
0.96	$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightarrow NO_{(g)} + H_2O_{(l)}$
0.68	$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{2(aq)}$
0.34	$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
0	$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$
-0.76	$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

Figure 11-4. Table of Standard Reduction Potentials

The redox reactivity of different chemical species is often tabulated according to standard reduction potentials for half-reactions. Any combination of half-reactions can, in principle, produce a spontaneous redox reaction; the direction of the reaction is determined by which half-reaction has the greater standard reduction potential.

Any pair of half-reactions can be put together to describe a redox process; if the reduction half-reaction in the overall reaction is more favorable according to the reduction potential, then the reaction will proceed as written. Otherwise, the reaction will proceed in the opposite direction unless current is applied. Keep in mind that in order for a redox reaction to occur, an oxidation must accompany the reduction. As we learned with the simple activity series, the components of a half-reaction may be either reactants or products in the overall process, and so one of the halves proceeds in reverse of how it appears in the table.

Tables of reduction potentials include numerical values with the qualitative ordering of the half-reactions. Just as one half-reaction cannot proceed without the other, a **potential difference** by definition requires a comparison of two energy levels. The difference between the energy levels influences how readily the electrons will move to achieve the more stable species in a reaction. Just as a ball rolling down a hill gains speed the higher up it starts to roll, electrons will move with more energy the larger the potential difference is between them. Reduction potentials are given in Volts (V), the unit for differences in electrical potential. A Volt is defined as 1 J/C, or one Joule of energy per Coulomb of charge, and so a difference in electrical potential can be viewed in terms of the energies of moving electrons. A spontaneous reaction is said to have a positive **electromotive force**, or emf. If a reaction proceeds without outside intervention, then the electrons will move with energy proportional to the difference in reduction potentials of the two half-reactions.

Figure 11-5. Reduction Potentials

Here, copper(II) ions react with zinc metal to produce a voltage of 1.027V, as seen on the meter. These are approximate results from an experiment as conducted in a laboratory.

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The difference between the *E°* values of the two halves gives a positive value for spontaneous processes. If we examine the reaction between zinc metal and copper (II) ions,

$$Cu^{2+} + Zn^{(0)}_{(s)} \rightarrow Cu^{(0)}_{(s)} + Zn^{2+}$$

we can see that the copper ions are undergoing reduction, but the zinc metal is undergoing oxidation. According to the table of reduction potentials, this is exactly as it should be; the reduction of Cu^{2+} to Cu has a reduction potential of 0.34V, compared to -0.77V for the reduction of Zn^{2+} to Zn. The difference between these two values represents the potential difference between the two half-reactions:

$$0.34-(-0.77) = 1.1V$$

Since this value is positive, the electrons move with 1.1 Joules of energy per Coulomb of charge. (Figure 11-5)

Although the reduction potentials are normalized per electron, the amount of charge carried over the course of a reaction is proportional to the number of electrons transferred, and to the number of moles of reactants consumed. This proportionality is one of Faraday's Laws, and it was from this proportionality that English scientist Michael Faraday (1791–1867) determined the amount of charge carried by one mole of electrons to be 96485 C/mol. This is known as Faraday's constant, F. This is an enormous amount of charge; but like any other conversion factor, it can be applied on any scale. Because Faraday's constant is normalized according to moles of electrons, it can be used in stoichiometric calculations.

Glossary

Electromotive force
The other term for the voltage associated with an electrochemical reaction.

Potential difference
Also referred to as "voltage," the work done by (or required by) a redox process to transfer electrons.

Standard reduction potential
For a reduction half-reaction, a value for the electromotive force or voltage generated when that half-reaction is paired with a standard electrode.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 5: Putting Spontaneous Processes to Work—Batteries

Charge can also be related to energy, which is central to applications of redox processes. The electrons cancel out in the final balanced equation, but they are critical in any calculations involving energy transferred in the reaction. We can recall from Unit 9 that the free energy of a process can be used to determine the spontaneity of the process, as well as provide an upper bound for the amount of work that the system will be able to do on the surroundings. The value of ΔG can be determined in a number of ways, including calculations based on *E*° and number of electrons. For both standard and nonstandard conditions, the following relationship:

$$\Delta G = -nFE^\circ$$

allows us to define emf in terms of energy, not just electricity. A positive emf will yield a negative ΔG, both of which are the sign conventions for spontaneity. If we wish to apply redox processes to do useful things, a large, negative ΔG is a good start! Keep in mind, as we discuss the various applications of redox reactions, that any application of redox (or any other type of chemistry, for that matter) will be influenced by several factors, not just the identities of the reactants and products.

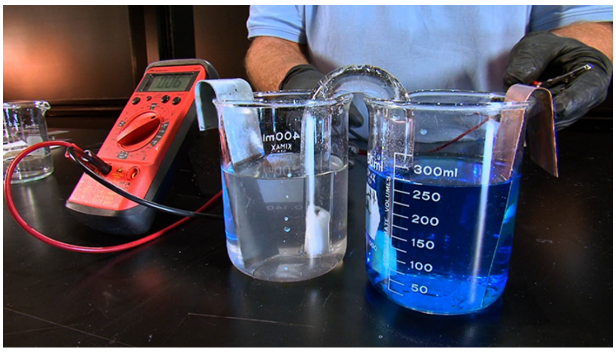


Figure 11-6. The Classic Galvanic Cell

The Cu/Zn reaction is set up in separate beakers with a salt bridge and wire connecting the two half-cells. The direction of electron flow is given above the wire, and the voltmeter displays a positive value for the cell emf, indicating a spontaneous reaction.

For electronic applications, the halves of a redox reaction are separated into two half-cells, the **anode** and the **cathode**. Reduction takes place at the cathode, oxidation at the anode; therefore, electrons flow from anode to cathode in a spontaneous reaction. In order for a redox process to generate usable current, the electrons must be forced to move through a wire. Charge balance must be maintained, so the half-cells must also be connected by a channel allowing ions to travel. Spontaneous processes set up this way are called "**galvanic cells**." The copper/zinc reaction from Section 4 is actually a classic benchtop example, called the "Daniell cell." In this setup, a copper wire in a solution of Cu^{2+} ions forms the cathode, and a zinc wire in a solution of Zn^{2+} ions forms the anode. A wire and a salt bridge (in this case, a tube packed with porous material and saturated with a solution of a nonreactive salt) are both used to connect the two beakers containing the electrode materials. If we include a voltmeter in the circuit, we can read the potential of 1.1V, as predicted by the difference in reduction potentials. (Figure 11-6)

Figure 11-7. Batteries

A selection of commercially available batteries for different personal-use applications is shown above. Many of these may look familiar as the power source for household items. Most of the ones pictured here are traditional alkaline batteries.

Although this is a great illustration of how a galvanic cell works, it is not very practical; most people would prefer not to carry two beakers of liquid just to power their phone. The Daniell cell can be built as a more compact, self-contained system, and of course other battery systems can be as well. The redox chemistry is only the beginning in the development of batteries, and often the ease of use and the cost of the materials end up trumping what might otherwise be perfectly effective chemistry in determining what reaction to use.

One of the biggest advances in the development of portable, safe batteries was simply developing battery systems that did not depend on containers of liquid. The batteries that we see advertised the most heavily, aside from car batteries, are the simple, disposable alkaline batteries—AA, AAA, 9V, etc. as shown in Figure 11-7. In an alkaline battery, the net reaction does not show much evidence of basic (or alkaline) materials:

$$Zn_{(s)} + 2MnO_{2(s)} \rightarrow Mn_2O_{3(s)} + ZnO_{(s)}$$

but the half-reactions reveal how alkaline batteries get their name:

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^- \text{ (anode)}$$

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^- \text{ (cathode)}$$

The construction of the battery requires a solution of hydroxide ions, but the solution is in gel form, rather than liquid. The battery materials are both cheap and environmentally benign enough that in some states, alkaline batteries can be thrown away in the trash. The materials are not inert, however; and so even a simple AA battery can be a potentially dangerous object. The battery discharges to a small extent even when not in use, and the discharge can generate gas-phase products. This builds up pressure in the container, which eventually breaks the container and allows the hydroxide solution to leak. This does not typically happen before the battery dies, and can be forestalled by keeping batteries cold until we use them; however, if we attempt to recharge a disposable alkaline battery, or keep them in a hot room, it's an entirely different—and possibly explosive!—story.

Glossary

Anode
In an electrochemical cell, the electrode at which the oxidation half-reaction occurs.

Cathode
In an electrochemical cell, the electrode at which the reduction half-reaction occurs.

Galvanic cell
An electrochemical cell in which the redox process involved occurs spontaneously.

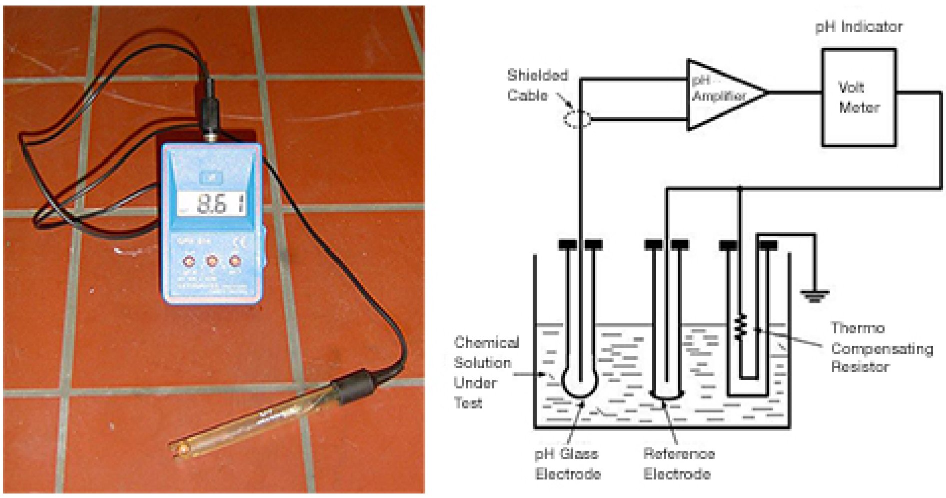
Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 6: Beyond the Standard Reduction Potential

Standard reduction potentials are extremely useful, but their numerical values apply strictly to systems at 25°C, with all gases at 1.0 atm pressure and all solutions at 1.0 M concentration. These conditions are generally unrealistic for the various applications of redox reactions. Not all of the deviations from standard conditions have the same effect, though; and so the determination of emf under nonstandard conditions requires a relationship that takes all of these possible deviations into account. This relationship can actually be summarized in a single, albeit large, equation, known as the "Nernst equation." Deviations from nonstandard conditions are not always detrimental, but they need to be taken into account for practical application of redox processes.

pH and Redox Reactions

No discussion of acid/base chemistry would be complete without measurements of pH and pH measurements can be made through redox reactions. Although litmus papers and indicator compounds can offer a rough estimate of the pH, a true measure, by definition, requires a measure of H^+ concentration. This is usually accomplished by the use of a pH meter, whose operation is based on measured differences in emf.



A pH meter and a diagram of the electronics inside. © Left: Wikimedia Commons, Public Domain. Right: Wikimedia Commons, CC License 1.2. Author: todd, 09 February, 2009.

The biggest influence on cell emf is deviation from standard-state concentrations; and in calculations, the concentrations (standard or otherwise) are encompassed in the reaction quotient, Q. If all the other variables are kept constant, then any changes in measured cell emf can be attributed to the changing reaction component. A pH electrode contains material for both halves of a redox reaction, in which one of the half-reactions includes hydrogen ions. The wires and the other chemical components are housed in a casing with a hydrogen-permeable membrane. When the electrode is placed into a solution, the measured potential changes according to the solution's H^+ concentration. The meter reads the signal from this measurement, and converts it (using the Nernst equation!) to a concentration, then to a pH.

We have seen that, at one extreme, a redox reaction can run to the point where it no longer generates current (as in a dead battery). In this situation, the reaction has reached a state of chemical equilibrium; neither direction of the reaction is favored and therefore the current-generating direction no longer predominates. At the other extreme, the initial setup of reagents to begin the reaction produces the highest measurable cell emf: As a reaction progresses, the amounts of reactants decrease. Since any deviations from 1.0 M concentration affect the reduction potentials and cell emf, it can be expected that consumption of reactants will ultimately decrease the actual potential difference between two half-cells.

If we look at a display of batteries in a store, we will see that alkaline batteries come in several shapes and sizes, as well as two different voltages. The AA, AAA, C, and D batteries are all listed as 1.5V. Are they just different sizes for different sizes of appliances? Not quite. We can recall from Section 4 that, although the reduction potentials are normalized per electron, the actual amount of charge carried depends on the number of electrons transferred in a reaction. Therefore, more moles of reacting species allow for more moles of electrons to flow. The larger batteries contain more reactant materials, and therefore are able to produce more current than the smaller batteries.

Figure 11-8. 9-Volt Battery

Batteries come in all shapes, sizes, and chemistries. In addition to adjusting the chemistry to produce a battery with a particular voltage, individual cells can be connected in a series to generate a larger voltage, as in the 9V alkaline battery.

What, then, makes a 9V battery a 9V battery if size alone does not change the voltage? When working with electronics, we sometimes connect electrical components in a series. In the case of batteries, the connection of multiple cells in a series produces a net voltage, which is the sum of the individual cell voltages. So, the chemistry of a 9V alkaline battery is the same as that of a 1.5V AA alkaline battery, but the physics are different: six individual 1.5V cells are connected in a series to generate the net 9V. (Figure 11-8)

Regardless of the size of the battery, or even the listed voltage, alkaline batteries do not last forever, and they are not rechargeable. As we will see in the next section, however, redox chemistry can be forced to proceed in the nonspontaneous direction. With the right kind of chemistry and a lot of engineering, various batteries have been developed that can be safely recharged. Pragmatically, the difference between a rechargeable battery and a nonrechargeable one is that the reactants in a rechargeable battery can be regenerated safely by the application of current to the battery. This has its limits, however; and ultimately, even a rechargeable battery will reach a point where it can no longer be recharged to full working capacity. Part of battery engineering is to develop materials that can withstand a larger number of charge/discharge cycles.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 7: Electrolyte Reactions and Corrosion Prevention

A dead battery is not always an irreversible situation. Any time we recharge an electronic device or jump-start a car, we force the battery's redox reaction to run in the nonspontaneous direction by applying current from an electrical outlet or another car. Processes that represent the nonspontaneous direction of a redox reaction are referred to as "**electrolytic**." Electrolytic processes will not run without the application of a voltage larger than that predicted for the reaction; but so long as that condition is met, the process is governed by stoichiometry. To drive an electrolytic process, the applied current must supply all of the electrons prescribed by the stoichiometric calculations for the system. In electrical terms, current is given in amperes (1 A = 1 C/sec); so the total time necessary to complete the process can be determined by calculating the total number of electrons needed and their corresponding charge, and dividing the result by the amperage of the available current.

Galvanization

Another means of using one redox process to prevent another, usually used specifically for rust prevention, is the use of sacrificial anodes. Recall from the activity series that some metals are more susceptible than others to oxidation. It turns out that several metals are more reactive than iron, and will therefore preferentially undergo oxidation if they are in contact with an iron surface. Many of these metals are inexpensive enough to be used at regular intervals around iron structures, then discarded and replaced once the metal has been completely consumed. For example, plates of zinc are often bolted to the hull of a ship. These plates will corrode while the iron hull of the ship does not, and then the zinc plates can be periodically unscrewed and replaced, a much cheaper and easier solution to having to replace rusted sections of the hull of an oil tanker.

Galvanized Nail. © Science Media Group.

Zinc coatings can also serve this same purpose on iron. In a process called "galvanization," zinc can be electroplated onto the surface of an iron object. This is often done on nails and other building materials that are made of iron that will be out in the elements with air and water. This coating both physically protects the inner iron surface as well as serves as a sacrificial anode to prevent its oxidative rusting inside.

If we look at the specifications for a laptop computer, we will likely see the term "lithium-ion battery." Occasionally, we may see "nickel-metal hydride" or even "nickel-cadmium," usually on batteries for toys and game systems that have to be replaced often. All three of these systems are rechargeable, and operate on exactly the chemistry that their names imply. The nickel-cadmium system is one of the original rechargeable systems, and is in many ways an excellent battery: It retains its original voltage almost until the point when it needs to be recharged. It can discharge quickly and therefore generate high-amperage current, and it can be recharged many times. Even though these nickel-cadmium batteries are inexpensive to make, there is a price to pay. Recharging them is not very efficient; the batteries get very hot during this process, wasting precious energy. Additionally, cadmium is an extremely toxic element. The other batteries have been developed using the same reversible chemistry premise of the nickel-cadmium battery, but with the goal of making them less toxic to make and dispose of, and to have lifetimes on the order of years. Even over the past decade, the batteries in laptops have become smaller and lighter, and can hold more hours of battery charge for longer periods of time. Batteries will continue to improve with more research and engineering.

Figure 11-9. Statue of Liberty

Pure copper oxidizes slowly, but copper objects left outside develop a greenish layer, called a "patina," over time. The exact composition of the patina depends on the environment to which the copper is exposed, but the resulting layer prevents the copper underneath from being oxidized further.

Most automobiles and boats use rechargeable lead-acid batteries, which are actually filled with plates of lead and lead(IV) oxide immersed in concentrated sulfuric acid. These batteries are actually 12V batteries made up of six 2V cells arranged in a series inside the battery. And while the lead is toxic, the materials are cheap and the batteries are usually recycled to auto shops to be used to make new batteries. These batteries are the best at producing very large currents, in a very short period of time, which is exactly what a starter motor of a car needs. However, these batteries are extremely heavy, which makes them impractical for use in space or in laptops. Also, these batteries can be very dangerous as high electrical current can be deadly. This is why the instructions for jump-starting a car are so explicit so that we can avoid electrocuting ourselves, or overheating the battery with the risk of spraying hot concentrated acid out of the battery.

Aside from reversing redox chemistry to recharge a battery, these reactions can be forced to "run backwards" in order to deposit a uniform layer of metal on an electrode, in a process known as "electroplating." Electroplating is often used to deposit an unreactive (or expensive) metal onto a core of a more reactive, or cheaper, metal. Therefore, the object to be plated serves as an electrode in the reaction. Gold is often plated onto silver for jewelry-making, and onto various metals for electronics:

$$Au^{1+} + e^{1-} \rightarrow Au_{(s)}$$

The drawback for this process is that many of the ways to set up this reaction use gold cyanide, which releases highly poisonous cyanide into the environment.

When a coating forms on the surface of a metal, like the dark color on copper piping or the green color of the Statue of Liberty, it is called a "patina." Patinas form when metals react slowly with their environment over time, usually in a redox reaction involving the oxygen in the air. This give antiques and old coins the warms colors we are used to, but it is not a bad thing because in many cases it leads to **passivation**. Passivation is when a coating, like a patina, forms on the surface of a metal, but now the rest of the metal is protected under this coating. These new surfaces, after being passivated, are more resistant to corrosion, are sometimes harder, and often improve the look of the surface. (Figure 11-9)

The corrosion resistance afforded by passivation can be viewed as one redox process preventing another. However, not all passivation processes protect the metal. While the oxide layer on aluminum or the patina on copper prevent any further reaction at the surface, the formation of tarnish on silver can actually penetrate into the silver and damage it beneath the surface. In the case of iron rusting, it turns out that a little bit of rust on iron actually increases the chance for further oxidation. This is the reason that one of the world's most famous iron structures, the Eiffel Tower, is constantly painted. This is to protect the iron-steel pieces that the tower is made of from being exposed to oxygen and moisture, so that they cannot rust.

Figure 11-10. Two Anodized Aluminum Carabiners

First, the surface of the aluminum was oxidized to create a dull coating of aluminum oxide, which then allows the surface to be dyed an array of colors. Thus, it protects the interior aluminum metal from further oxidation and provides an aesthetic surface.

Passivation is not only achieved through natural processes. Electrochemical treatment of metals is not limited to electroplating; any metals can be **anodized**, which is a form of unnatural passivation. Anodization applies to several different processes, all of which involve the metal as the anode in a redox reaction. Aluminum is often the target of anodization: The metal itself is relatively inexpensive, and it can be electrochemically modified in a variety of ways, including the formation of an aluminum oxide coating. Aluminum oxide forms readily but slowly without outside intervention, but the controlled formation of the oxide produces specific thicknesses, and this can be followed up with dyeing or further sealing of the layer. The controlled layer is then resistant to further oxidative reactions. Other metals are often anodized as well, both for pragmatic and aesthetic purposes. (Figure 11-10)

Glossary

Anodization
The description of a modified metal surface through reaction with another chemical component, forcing the metal surface to undergo oxidation (i.e., act as an anode).

Electrolytic cell
An electrochemical cell in which the redox process is forced to run in the nonspontaneous direction.

Passivation
The natural oxidation of a metal surface by exposure to other chemical species, so that it is prevented from further oxidation.

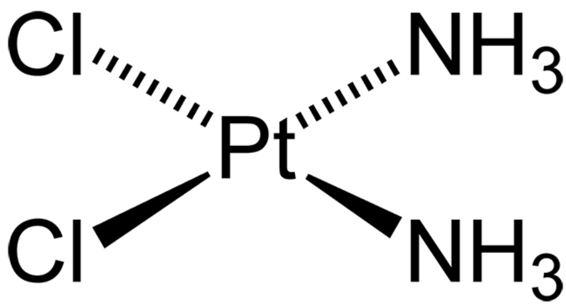


Figure 11-11. The Structure of Cisplatin

The central platinum metal atom has four coordinate covalent bonds to two chloride ions and two ammonia molecules, making a coordination complex that has a square planar geometry. Because this molecule is flat, the two chlorines could be next to each other or they could be across from each other on the metal. However, if they were across from each other, that would make a different isomer called "trans-platin."

Physiological processes and pharmaceutical advances have generally been assumed to be the domain of organic chemists, biochemists, and biologists. Metal-containing compounds, however, are essential parts of several important pharmaceuticals and biologically important molecules such as hemoglobin, which will be discussed in Section 11. Another such compound is Cisplatin, or *cis*-diamminedichloroplatinum(II), a successful chemotherapy agent, especially against testicular cancer. The compound consists of a platinum ion (Pt^{2+}) with two chloride ions and two ammonia molecules. However, this is not an ionic compound like sodium chloride where the sodium cation (Na^{+}) and chloride ion (Cl^{-}) are attracted to each other by the coulombic forces due to their charge. Nor is it a shiny piece of metal in its native state as in a coin. In this case, the very electropositive metal ion shares the electrons from the lone pairs of the electron-rich chloride ions and the ammonia molecules in a type of covalent bond called a "**coordinate covalent bond**." This results in a coordination compound or complex where a metal ion in the center is bound to small molecules called "**ligands**." Anything with a lone pair can act as a ligand for a metal ion to make a coordination complex. Even the oxygen that we breathe in binds to the iron in hemoglobin in this same fashion. The two chloride and the two ammonia ligands arrange themselves around the platinum ion in a square plane, as can be seen in Figure 11-11.

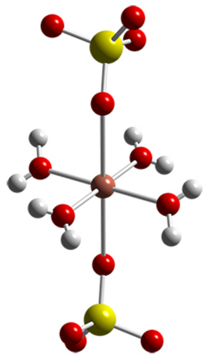


Figure 11-12. Copper(II) Sulfate Pentahydrate

The copper ions in copper(II) sulfate pentahydrate are actually in an octahedral arrangement. There are six ligands that share their electrons with the copper metal through their oxygen atoms. The complex ion that forms is what gives copper(II) its blue color.

In Unit 5, we learned that valence shell electron pair repulsion theory (VSEPR) explains how small molecules with main group central atoms make shapes based on how many lone pairs and atoms are attached to the central atom. For transition metals, their coordination complexes can form some of these same shapes. It is beyond the scope of this unit to show which coordination complexes would be which shapes, but we can say that transition metals most commonly have six ligands attached to them, and they form an octahedral arrangement. Figure 11-12 shows copper(II) sulfate pentahydrate crystals, as well as the octahedral structure of the copper ion with its six ligands attached. The second most common coordination for transition metals is to be bound to four ligands, but in this case there are two options for the geometry: square planar like the cisplatin or tetrahedral like the $[NiCl_4]^{2-}$ ion, which is greenish-yellow in color.

Nickel Hydrazine Perchlorate: An Explosive Material

What happens when a single compound contains both an oxidizing agent and a reducing agent? This is likely to be a very reactive compound. Now what happens when a graduate student makes 10 grams of the compound, instead of the 100 milligrams that his advisor instructed him to make; that's 100 times more than expected. Afterward, the graduate student placed this brilliant purple powder into hexane, a flammable solvent and began to grind it in a mortar and pestle, all without the protection of safety goggles or a blast shield. Is this the plot of a bad movie? No. This scenario played out—miraculously with no fatalities—in a Texas Tech University research lab whose specialty is explosive compounds.[1] The compound in question, listed in the graduate student's notebook only as "nickel hydrazine perchlorate," would be an extremely reactive, shock-sensitive compound. Suffice it to say that the graduate student's attention to lab safety reads more like a list of what *not* to do.

Nickel(II) ions, like all transition metal ions, like to bind to small molecules to serve as ligands, and then they form coordination compounds. Both the perchlorate ion and the hydrazine molecule are known to donate their electrons to electron-poor metals and serve as ligands. The perchlorate ion, ClO_4^-, and its compounds are classified as strong oxidizers, and are therefore very hazardous. The chlorine in the perchlorate ion is in a very high oxidation state (+7); and so in the presence of a reducing agent, it will readily accept electrons. The salt, ammonium perchlorate, is even used in solid rocket fuel; also, most perchlorate salts are dangerous to store because they are shock sensitive and can explode when dropped or jostled.

On the other hand, hydrazine is a good reducing agent, and one of the main chemicals used as rocket fuel. By having nickel ions around, a strong oxidizer and a strong reducing agent have been brought together into one compound. So, there is a very spontaneous and exothermic reaction waiting to happen, which with a small shock, such as the motion of a mortar, can initiate an explosive redox reaction. In this case, the reaction, once it began, created a small explosion that blew up a portion of the laboratory. Although the graduate student lost three fingers and had serious eye damage, he survived. Because of this incident in 2010, an investigation ensued, and new procedures and protocols are in place across the country.

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[1] http://www.depts.ttu.edu/vpr/integrity/csb-response/the-accident.php

What makes transition metals different from elements on the other parts of the periodic table is that their valence electrons are in a set of *d* orbitals. When transition metals form coordination compounds, all of their valence electrons, even those that were in the *s* orbital, move into the 10 available spaces in that *d* subshell. This is also why transition elements are called the "*d*-block elements." When the valence orbitals are in the *s* or *p* block, the possible oxidation states are very limited. For example, fluorine always will make an F^- ion, and calcium will always make a Ca^{2+} ion. However, transition elements usually have several common and a few less common oxidation states. Iron is commonly found as iron(II) or iron(III) ions, and chromium as chromium(II), chromium(III), or chromium(VI). We can find transition elements with oxidation states that are even as high as +8, which is seen in compounds of osmium, a rare element that is important in oxidation reactions in organic chemistry.

Because transition metals have a wide variety of possible oxidation states, they are also very active in redox chemistry, especially in biochemistry, as will be seen in Section 10. They also tend to be highly colored, and different oxidation states have different colors partially due to the different numbers of *d* electrons each transition metal ion has. Let's consider iron again; it is in Group 8 on the periodic table and thus has eight valence electrons. When we have iron(II) ions with a +2 charge, two electrons are removed, which means there are six electrons in its *d* orbitals. If we do the same thing for iron(III), we can see that Fe^{3+} ions have five *d* electrons. In the next section, we will see how these *d* electrons play a key role in the colors that these compounds display.

Glossary

Coordinate covalent bond
A covalent bond between two atoms where one of the atoms provides both electrons that form the bond. This usually takes place between a ligand and a metal cation.

Ligand
An ion or molecule that binds through a coordinate covalent bond to a central metal atom to form a coordination complex.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 9: Colorful Chemistry

If we step into an art studio or artists' supply store, we will see metal names in many of the paint colors: cobalt blue, cobalt green, cadmium yellow, and even titanium white. Unlike many main-group compounds, many transition metal compounds are intensely colored. Several metals appear in multiple pigments, though. How can one metal be responsible for so many colors? Actually, the metal needs a little help from what's bonded to it.

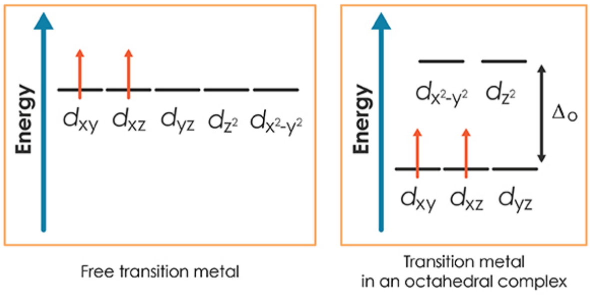


Figure 11-13. Ligand Field Splitting

The orbitals in a *d* subshell are usually all the same energy, but in transition metal compounds, the energy levels split. Electrons can be promoted from the lower energy levels to higher energy levels when the compound absorbs light of an appropriate energy, delta octahedral (Δ_o) in this case.

We have seen some examples of colorful chemistry already. Recall from our discussion of atomic emission spectra that atoms emit light, often in the visible region of the spectrum, when they are forced into an excited state and allowed to return to the ground state. The wavelengths of the emitted light correspond to electronic transitions; larger separations of energy correspond to shorter wavelengths of emitted light, and vice versa. Electronic transitions are responsible for the colors of transition metal compounds, too, albeit in a slightly different fashion. As we saw in Section 8, the *d* electrons heavily influence transition metals' patterns of reactivity; they will also have an effect on the colors of the compounds they form. As with excited atomic emissions, each metal will give different colors, just like neon light gave a red glow while a sodium arc lamp glowed yellow.

Titanium White and Zinc Oxide

For all the colors of the transition-metal pigments, titanium white is a bright, rich white pigment, but it has no color even though it has a titanium transition metal present. Why? Titanium certainly has *d* orbitals in its valence shell as a transition metal. The pigment in titanium white, however, is titanium dioxide, TiO_2. Titanium dioxide is actually one of the largest production industrial chemicals in the world, both as a pigment, and for other uses such as a food additive or sunscreen component. If we apply our rules for calculating oxidation states (oxide ions are -2, therefore the titanium must be +4) and then look at the position of titanium on the periodic table in Group 4, we can see that a +4 ion means that titanium has no electrons left in its valence *d* orbitals. Since there are no electrons present to absorb visible light by getting excited, the titanium dioxide reflects all of the wavelengths of visible light. What happens when we recombine all the wavelengths in the visible spectrum? We get pure white light.

There is another white pigment that was used long before titanium white called "zinc white," or "zinc oxide." We still see it being used today as a powerful sunblock, especially on noses of lifeguards where we just see a giant smear of white that blocks the sun and never gets absorbed by the skin. Zinc oxide has the formula ZnO, and since oxide ions are -2 charged, the zinc ion must be +2. Zinc is in Group 12, so with two electrons missing it has a full set of *d* electrons. So, why is zinc oxide also white? Since all 10 slots in the *d* orbital block are filled, even though there are lots of electrons present, none of them can absorb light and get excited because there are no empty *d* orbital spaces for them to move up into. So, just like the titanium dioxide, if the transition metal compound cannot absorb visible light, it reflects all the wavelengths and appears white.

In a ground-state electronic configuration, the five orbitals of the *d* subshell are degenerate or have equivalent energies. When ligands bond to a transition metal, however, the metal's *d* orbitals split into at least two different energy levels. Figure 11-13 shows how the five *d* orbitals split into a set of two and a set of three orbitals when a transition metal is in an octahedral coordination compound. The new gap in energy between these two sets is called "delta octahedral" (Δ_o) and is the energy of light that this molecule would have to absorb to jump an electron from the lower set of orbitals into the upper set. What affects the color of a transition metal complex is that the gaps between these sets of *d* orbitals have energies that fall in the visible region of light. It does not matter what geometry the transition metal coordination complex has, as even tetrahedral and square planar will have their sets of five *d* orbitals split, but in ways that differ from the octahedral case shown in Figure 11-12.

What are the factors that affect the color of a transition metal complex? First of all, the identity of the metal and the charge on the metal will have an effect on the wavelength of visible light that the complexes will absorb. The geometry of the complex, if it is octahedral or tetrahedral, and so on, matters. The ligands themselves also have a great effect. Figure 11-14 shows that a series of compounds of nickel(II) ions in water have wildly different colors depending on which ligands are attached to the metal ion.

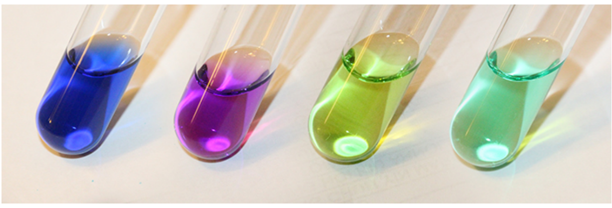


Figure 11-14. Coordination Complexes of Nickel

From left to right: $[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(H_2O)_6]^{2+}$. Note how changing the number of ligands and the identity of the ligands on nickel(II) ions can create an array of different colors, as the energies of the possible electronic transitions of the *d* electrons are affected by the changes in the ligands.

By absorbing some visible light, transition metal complexes reflect only part of the visible spectrum back to the human eye. Since the human eye is not a fancy spectrophotometer machine, it only has three simple color sensors called "cones" that can detect red, green, and blue light. So, if a compound absorbs red light, the OYGBIV (orange, yellow, green, blue, indigo, and violet) lights all reflect back to the human eye, but we don't see a crazy mix of all those colors. The human brain interprets color much more simply, and a color wheel is all we need to understand what the brain and eye will do to process light into color. On a color wheel, every color has a complementary color exactly across from it on the wheel (Figure 11-15). Red's complement is green. So, if a compound absorbs red light, the reflected wavelengths of light that reach the eye will be interpreted by the eye as just green light, even though it is a mixture of many wavelengths. In the same way, white light is really just a perfect mixture of all the possible wavelengths, and black is the absence of any visible light reaching the eye.

Figure 11-15. A Color Wheel

The colors in the visible spectrum are absorbed by a colored object, and the rest of the visible light is reflected. This light is absorbed because of the possible electronic transitions in the compounds. If a compound absorbs green visible light, the remainder of the visible spectrum heads toward the eye, and the brain interprets this as the color opposite it on the color wheel. So, a compound that appears red to the eye absorbs green light.

Transition metals can give color to matter even if they are present only in small quantities. In crystalline oxides of silicon and aluminum, for example, depending on where the minerals formed, some of the aluminum atoms can be replaced by trace transition metals. So, aluminum oxide, or corundum, which is nine on the Mohs hardness scale just below diamond, is a colorless, very hard stone. However, if a very small percentage of the aluminum atoms have been replaced by chromium(III) ions, this corundum will have a brilliant red color, and we call that a "ruby." On the other hand, if there were trace amounts of iron ions replacing some of the aluminum, the gemstone would look brilliant blue, and we would call it a "sapphire." Rubies and sapphires are identical in their chemical structure, with just a small trace transition metal impurity lending the gemstone color.

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 10: Metal Biochemistry

While the cisplatin is an example of adding non-natural transition metal complexes into a body, the role of metals in biochemistry is apparent from looking at the nutrition label on a cereal box. The nutrients include the macronutrients, like fats and proteins, with smaller amounts of vitamins and minerals. The minerals supply metals, including a few transition metals, and even vitamin B12 has a cobalt ion at its core. Although many of these are considered "trace" nutrients, they are nonetheless important in particular physiological processes. The coordination chemistry we have learned about earlier in this unit with smaller molecules extends to bioinorganic systems. In addition, the redox behavior of metals is essential in bioinorganic chemistry, as regular organic compounds containing only carbon, hydrogen, nitrogen, oxygen, sulfur, and phosphorus cannot undergo the types of specialized redox reactions that metals can, which are essential for life.

One of the best-known transition metal compounds in biology is hemoglobin. Hemoglobin is a large protein molecule, which has a heme group attached within it, and that heme group's ring serves as a ligand to bind an iron ion. Figure 11-16 shows how the oxygen molecule binds as a ligand to one site on the iron, while the heme ring and a histidine amino acid also serve as ligands. An iron in hemoglobin carries oxygen from the lungs to the bloodstream, and therefore it can be found in either the oxygenated or the deoxygenated form. The presence or absence of oxygen is sufficient to change its light absorption behavior, and therefore the color, of the compound. This should not be a surprise, because we learned in Section 9 that changing the ligands attached to a transition metal complex will change its color.

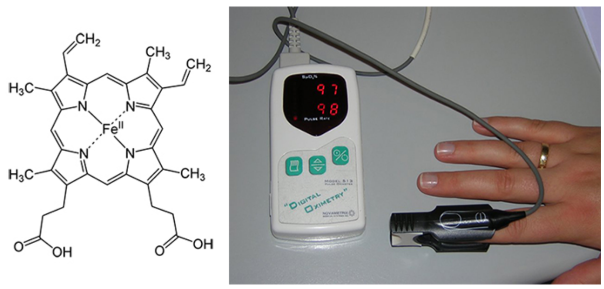


Figure 11-16. Hemoglobin

The heme group in hemoglobin bonds to oxygen in the bloodstream. The oxygenated and deoxygenated forms of hemoglobin have different colors, and so the oxygen content in blood can be measured spectroscopically using a pulse oximeter.

Because of this change in color, the oxygen content of blood can be measured noninvasively with a pulse oximeter—a miniature spectrometer that fits over a fingertip. Although oxygen binds readily to the heme group, so do other ions and neutral molecules that can also serve as ligands. In cases of exposure to carbon monoxide gas or cyanide ions, the CO or the CN^- binds more readily than the oxygen, which in turn blocks oxygen from being transported to the rest of the body. To some extent, the effects can be reversed by treatment with high pressures of pure oxygen in the case of carbon monoxide; but the cyanide is such a strong ligand, it permanently binds to the hemoglobin leading to death. Also, once cyanide binds to hemoglobin, it becomes a much bluer color, which is why patients in hospitals with an overly blue tinge to their complexion are called "cyanotic." This can happen due to exposure to cyanide or due to very low oxygen levels in the blood.

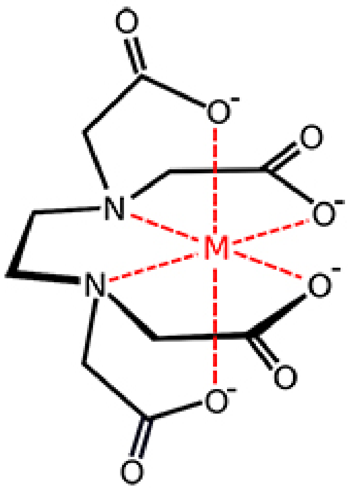
Iron appears in a number of other biomolecules; many of these compounds are the critical components of redox-active enzymes. Many physiological processes involve electron transfer and molecules like cytochrome P450 and ferredoxin, both of which contain iron ions, and are often required in the redox chemistry. The iron inside of cytochrome P450 is also inside a heme ring, but ferredoxins have clusters of iron ions and sulfur atoms inside them. Ferredoxins participate in both plant and animal biological processes; in humans, ferredoxin-1 provides an electron transfer conduit for the synthesis of thyroid hormones. Ferredoxin-1's alternative name, adrenodoxin, hints at this.

Iron isn't the only transition metal found inside enzymes in the body. Nickel ions can be found in a class of enzymes called "ureases," and humans have an enzyme called "catalase," which contains both copper and zinc atoms. While we're unlikely to see the effects of the urease enzyme in our daily life, any time we treat a cut with peroxide we see catalase in action. Catalase turns hydrogen peroxide into water and oxygen, which is why it bubbles when we pour it over a cut. The enzyme is present in the fluids in the body in order to destroy any peroxide that might get made, because it is a strong oxidant that can attach to other biological molecules.

Polydentate Ligands

Coordinate covalent bonding can occur through any lone pair, even one from a large molecule. For example, the lone pairs on the bases found in DNA can bind to the platinum in cisplatin, which explains how it ultimately inhibits cancer cells from reproducing. In addition, more than one lone pair on the same molecule may bond to a metal. When one molecule donates more than one lone pair to a metal, the molecule is referred to as a "polydentate ligand," literally meaning "having many teeth" in Latin. Commonly, a small molecule has two sites that can bind to the metal yielding a bidentate ligand. The oxalate ion, which can be found in certain foods like rhubarb, is a bidentate ligand. Some large molecules can act as polydentate ligands, wrapping themselves around the metal in a process referred to as "chelation," which comes from the Greek for "claw," since the ligand acts like a pincer. The heme ring around iron in hemoglobin, and the ring in Vitamin B12 that holds the cobalt, are both examples of polydentate ligands.

A commonly used polydentate ligand is ethylenediaminetetraacetate, which can bond to the same metal atom through up to six atoms. The name is a huge mouthful, and so it is usually abbreviated to a much more commonly known acronym: EDTA with a -4 charge. The ability of EDTA to bind so strongly to so many different metals has led to an array of applications. Because it can bind to small ions like calcium and magnesium, it is commonly used as a water-softening agent. Because it can bind strongly to all of a metal's coordination sites, it can be used to render metals unreactive and prevent unwanted reactions. Heavy metal poisoning is therefore often treated with EDTA, and this treatment in a hospital is called "chelation therapy." EDTA is also used in preservatives of various food, personal care,



EDTA. © Wikimedia Commons, Public Domain.

and medical care products, as the removal of metal ions prevents oxidation of other components and inhibits the uptake of essential metals into bacteria.

Another of the critical transition metals is the cobalt in vitamin B12. The vitamin has a ring structure similar to a heme group, but the central metal ion is cobalt instead of iron. Although the recommended daily intake of the vitamin is only a few micrograms, B12 is involved in a huge range of biological processes. The metal center facilitates a number of different processes, most notably the metabolism of fats and proteins and the production of myelin, a protective coating of nerve cells. Several different forms of the vitamin, including different oxidation states of the cobalt, when combined with folic acid, are essential in promoting good heart health and proper fetal development in pregnant mothers.

Not all transition metal ions in biological situations are doing redox chemistry; in some cases, they are useful structurally to control the shapes of proteins. Other times, they are useful because ligands like to bind to them, and they can serve as an active site where non-redox chemistry takes place. For example, zinc is found in both aminopeptidase and carboxypeptidase enzymes. Both classes are critical to the digestion of proteins, and the latter is critical to the synthesis of various proteins, including insulin and blood-clotting factors. Zinc is also found in liver alcohol dehydrogenase, which begins with the coordination of the alcohol molecules to the zinc through the lone pair on the oxygen. However, the redox chemistry done by this enzyme uses a cofactor called NAD^+, as the Zn^{2+} ion cannot spontaneously do redox chemistry.

CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 11: Conclusion

Metals can do far more than just transfer electrons. They also play a major role in the generation of electricity, so much so that they even appear in biological systems to aid in physiologically relevant electron transfer processes. An understanding of redox activity is the basis for all sorts of engineering, whether it's optimizing the contents of a battery, improving the durability of a metal structure, or even forcing nonspontaneous chemical processes to occur.

The chemistry of the transition metals is a far broader topic than discussed here, but, like all other branches of chemistry, it follows patterns. Some of the simplest versions of these patterns actually go a long way toward explaining some of the most relevant chemistry of the metals. Redox is only the beginning, and we will see some of the other roles that metals can perform in Unit 13 when we learn about alloys.

CHEMISTRY
CHALLENGES AND SOLUTIONS

Unit 11: *The Metallic World—Electrochemistry and Coordination Compounds*

Section 12: Further Reading

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