

Faculty of Science

**Unit 6:
Electrochemistry**

CHEM 1523
Principles of Chemistry

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Unit 6: Electrochemistry

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Unit 6: Electrochemistry

Overview

Unit 4 of this course examined proton-transfer reactions. This unit is about reactions involving transfers of electrons. Such reactions are known as **oxidation-reduction** reactions or, more simply, **redox** reactions. Oxidation is the loss of electrons; reduction is the gain.

In the late sixteenth century, William Gilbert, a physician at the court of Queen Elizabeth I, experimented with static electricity. He produced electric charges by running rubber over fur. His deduction from these experiments was that there are two kinds of charge: the “like” kind repels while the “unlike” kind attracts. (You should be able to think of numerous examples of this static electricity. Clothing taken directly from a drier is one example. On very dry days you can get a static shock from sliding across a car seat and then reaching quickly to open the door. Vigorously stroking a cat and then touching something with your fingertip has a similar effect.) In the mid-eighteenth century, Benjamin Franklin gave names to the two different types of charge. The charge on the fur was considered **positive** and the charge on the rubber, **negative**.

The French physicist, Coulomb, proposed the law that now bears his name: the attractive or repulsive force between two electrically charged species is directly proportional to the product of their charges and indirectly proportional to the square of the distance between them. That charge separation involved some sort of movement of charged species was first noted by another French physicist, Ampere. In electrochemistry, you will find that Coulomb and Ampere are remembered in the form of names of electrical units. The unit of electrical charge is the **coulomb** and the unit of electrical current is the **ampere**.

This unit deals with reactions where electrons are transferred from one substance to another. These oxidation-reduction reactions, as they are called, can take place whenever an electron donor substance is mixed with an electron acceptor. In this sense, electron-transfer reactions are similar to the proton-transfer reactions discussed in Unit 4. The reaction proceeds spontaneously in whatever direction leads to a lower free energy. In electron-transfer reactions, the electron-donating substance can be kept in a location physically separate from the electron-accepting substance. This arrangement is called a **cell**. When a reaction is carried out this way, the electrons can get from the donor to the acceptor only by passing through an external electrical conductor. If a lamp or a motor is placed in this external conductor, some of the free energy of the reaction can be converted into useful work.

Many electron-transfer reactions do not take place spontaneously because their reactants have a lower free energy than their products; ΔG is positive. An external battery or power source placed in the circuit between the two parts of the cell acts as an “electron pump” and forces the electrons to a higher free energy. During such a reaction electrical energy is converted to chemical energy. This process is called **electrolysis**. Within a cell the electric charge is carried by positive or negative ions. These may be in aqueous solution or in a molten salt. Substances containing ions that are able to move under the influence of an electric field are called **electrolytes**.

The name associated with the early investigation of electrolysis is that of Michael Faraday. In the early 1830s, Faraday published the results of his studies on the relationship of quantity of electricity to the stoichiometry of the reaction. These results form the basis for **Faraday’s laws**, which you will be considering in this unit. The electrical unit named after him, the **faraday**, is the total charge on a mole of electrons, a value of 96,500 coulombs. Faraday was the apprentice/pupil of Sir Humphrey Davy. Davy’s electrolysis of molten NaCl and of molten KCl in the early 1800s led him to discover the alkali metals, sodium, and potassium, and to become the first electrochemist.

Electrolysis has important commercial applications. In British Columbia, there are numerous industries dependent on electrolytic processes, for instance, the refining of aluminum. The production of metallic aluminum involves electrolysis of molten aluminum salts. Aluminum is the third most abundant element in the earth’s crust. Its use as a structural material is due to its strength, lightness, and relative resistance to corrosion. The electrolysis of aluminum is still based on the process worked out in 1886 by Charles Hall, a 22-year-old chemistry graduate student. Hall found that a mixture of Al_2O_3 with cryolite (Na_3AlF_6) melted at about 1000°C . Electrolysis of this molten mixture produces pure aluminum metal at the cathode. (By itself, Al_2O_3 melts at 2000°C .) Today, other materials that lower the melting point even further are used. The required Al_2O_3 is obtained from purification of bauxite ore. The Hall process requires abundant electrical energy because of the thermodynamic stability of the aluminum oxide ore. In fact, approximately 4% of the electricity generated in North America is used to produce aluminum. It is cheaper to transport the bauxite to the source of the electrical energy than to transport the electricity to the ore source. Thus, bauxite is imported into BC, usually from Jamaica to Kitimat, where abundant electrical power is available for the electrolytic process. Another metal refined by electrolytic means in British Columbia is zinc, at Trail.

Electrolysis is also important, indirectly, to the forest products industry. Chlorine gas is used as a bleaching agent in pulp and paper manufacture. This chlorine is produced in BC by electrolysis of brine (an aqueous solution of NaCl).

Sea water is not normally used for this purpose because it contains ions other than the Cl^- and Na^+ . Valuable commercial by-products from this method of chlorine production are NaOH and hydrogen gas.

In the late 1700s and early 1800s, Italians Galvani and Volta investigated the effects of electrochemical cells that produced electrical energy from chemical energy. These cells are known as **galvanic** or **voltaic** cells. (The first was produced by Volta in 1800. The potential difference produced by such a cell is still measured in units of **volts**.) In this unit, you will be expected to devise, theoretically, such cells based on a variety of redox reactions and to calculate their cell potentials.

This unit also examines the effects of oxidation-reduction in everyday reactions. Metals will not oxidize when stored under vacuum, isolated from the environment. Oxides, hydroxides, and sulphides of most metals have lower free energies than the pure metals (such metals are considered to be ores rather than pure metals). Once refined, the metal inevitably returns to the more thermodynamically stable, ore-like compound. This process is called **corrosion**. Some metals, such as the noble metals (e.g., gold, silver, and platinum), are resistant to corrosion. Others, such as aluminum, form a passive film at the surface, thus preventing further reaction by atmospheric oxygen. Metals such as iron and zinc are subject to widespread rather than localized surface corrosion. This unit discusses the electrical and chemical nature of corrosion and rusting.

Living cells extract their energy from certain redox reactions by coupling these with the synthesis of the energy-rich compound adenosine triphosphate (ATP). The mechanism of this “oxidative phosphorylation” is complicated and not yet completely understood. However, it is well established that when a reduced metabolite is oxidized by oxygen during cell respiration, a sequence of several distinct reactions is involved. A series of electron carriers is used between the primary metabolic reductant and the terminal oxidant, O_2 . This unit touches briefly on this electron transport chain. If you continue your studies in the field of biochemistry, the basic electrochemical principles introduced in this unit will help you understand such biological oxidation-reduction reactions.

Learning Outcomes

Once you have finished this unit, you should be able to:

- Balance oxidation-reduction equations.
- Write the oxidation and the reduction half-reactions for any redox equation.
- Perform calculations from redox titrations.
- Draw a cell diagram or a cell notation for the electrochemical cell based on a given redox equation.

- Deduce standard cell potentials from tables of standard reduction potentials.
- Calculate non-standard cell potentials using the Nernst equation.
- Calculate ΔG and K values from the appropriate electrochemical data.
- Calculate cell potentials for concentration cells.
- Do Faraday's law calculations.

Oxidation-Reduction

Study Section 4.4 in your textbook. Before you continue working through the rest of this unit, it is essential that you understand the terms discussed in the following paragraph.

Oxidation is the loss of electrons. A substance that causes oxidation is an **oxidizing agent**. **Reduction** is a gain of electrons. A substance that brings about reduction is a **reducing agent**. If you lose electrons you have to lose them to something, in other words, if one substance loses electrons then some other substance has to gain them. This means that oxidation cannot occur without the same amount of reduction occurring somewhere else. An oxidizing agent brings about oxidation by itself accepting electrons. It is reduced. Similarly, a reducing agent is itself oxidized. If you understand that the amount of oxidation must equal the amount of reduction occurring, then you have grasped the main concept behind oxidation-reduction (commonly abbreviated to redox) reactions. *The number of electrons lost must equal the number of electrons gained.* The terms *oxidation* and *reduction* originated long before electrons were ever imagined. The combination of an element with oxygen (combustion) can be regarded as a partial transfer of electrons from the element to oxygen. The term *reduction* is used to mean the reverse process, where a sulphide or oxide ore was reduced to the pure element.

Although we have just stressed that oxidation cannot occur without reduction (and vice versa), it is often useful to separate out the reduction half of a reaction and the oxidation half of a reaction. As the textbook shows, you can tell if you have a half-reaction since electrons appear on one side of the equation. In a full redox equation the electrons balance out on each side. Notice that each half-reaction is balanced for elements and has the same charge on each side.

Oxidation Number

You should be able to assign an oxidation number to any atom in a compound. Although it is an artificial concept (chemists, not atoms, do the assigning of oxidation numbers), it does provide you with a quick way to identify what is being oxidized and what is being reduced.

Another rule of thumb is that addition of oxygen or removal of hydrogen constitutes oxidation. Removal of oxygen or addition of hydrogen can be labelled as reduction.

In this section, memorize the rules for assigning oxidation numbers. This should not be very time consuming because you have already studied many oxidation number rules (although you may not have called them that) in Unit 1 of CHEM 1503, where you learned to name inorganic compounds. Try Example 4.5 in your textbook and its practice exercise. Read about periodic variation of oxidation numbers. An understanding of Figure 4.10 in your textbook may help you with oxidation number rules, but you do *not* need to memorize details from this figure.

Types of Redox Reactions

You do not have to memorize any of these specific reactions, but for each equation given, you should understand how the oxidation number was assigned, and you should be able to work out which element is being oxidized and which is being reduced. You will have already come across combination, decomposition, and displacement reactions (see Unit 1 of CHEM 1503), but may not have seen a disproportionation reaction where the same element is both oxidized and reduced. Make sure you can identify a disproportionation reaction. Work through Example 4.6 in your textbook and its practice exercise.

Balancing Redox Equations

Study Section 18.1 in your textbook. This unit examines two methods of balancing redox equations: the oxidation number method and the ion-electron method (sometimes called the half-reaction method). You can probably survive in this course using only one method, but there are advantages to both, and once you have mastered one method the other takes very little extra work to understand. Your textbook covers the ion-electron method in detail.

Oxidation Number Method

This method of balancing redox equations assumes that you already know how to assign oxidation numbers. The process requires you to:

1. Decide which element has increased its oxidation number and by how much, as well as which element has decreased its oxidation number and by how much.
2. Balance out the increase in oxidation number of one element with the decrease in the other (number of electrons lost equals the number of electrons gained).

Again, the best thing to do to help you grasp this method is to practise it. You will find that your proficiency in balancing redox equations is directly proportional to the practice you do. One nice thing about this sort of problem is that you always know if you are right because a correctly balanced redox equation will be balanced for mass and charge.

Work through the following problems.

Problem: Balance the following equations using the oxidation number method.

- $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{Fe}^{3+} + \text{H}_2\text{O}$
- $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$
- $\text{Cu} + \text{NO}_3^- + \text{H}^+ \longrightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$
- $\text{HClO}_4 + \text{Pb}(\text{NO}_3)_2 + \text{HNO}_3 \longrightarrow \text{HClO}_2 + \text{Pb}(\text{NO}_3)_4 + \text{H}_2\text{O}$
- $\text{Zn} + \text{BrO}_4^- + \text{OH}^- \longrightarrow \text{Zn}(\text{OH})_4^{2-} + \text{Br}^-$

Solution:

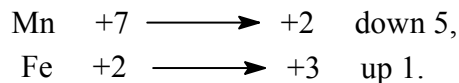
- If you check the oxidation numbers of all the elements on each side of the equation, you will find that the only two elements that change their oxidation numbers are Mn and Fe.

Mn has an oxidation number of +7 in MnO_4^- and +2 in Mn^{2+} .

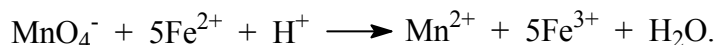
Fe has an oxidation number of +2 in Fe^{2+} and +3 in Fe^{3+} .

(With some practice you will not have to check all the oxidation numbers of all the elements. You will quickly be able to pick out where the oxidation number is increasing or decreasing.)

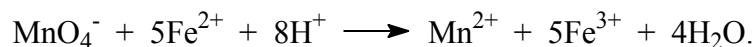
This change in oxidation number can be written as:



To account for the change in oxidation number, the ions containing the Fe atom are multiplied by 5. This gives an equation balanced for the oxidation-reduction portion:

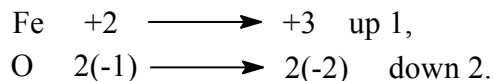


The only thing left to do is to balance for hydrogen and oxygen. There are four O on the left-hand side. You will need $4\text{H}_2\text{O}$ on the right-hand side. This means having a total of 8H^+ on the left. The balanced equation is now

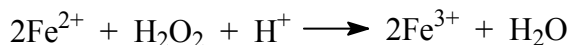


Note that the charge on each side is +17.

- b. The change in oxidation number can be written as:



In the H_2O_2 molecule there are two atoms of oxygen where the oxidation number is changing. You have to account for this in the oxidation number change. Now multiply the species containing Fe by 2.

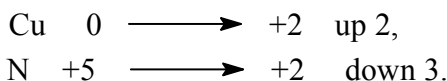


This equation is balanced for oxidation-reduction. Now balance for hydrogen and oxygen atoms by adding another H^+ to the left.

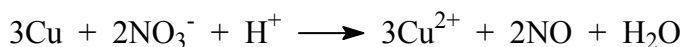


The charge on each side is +6.

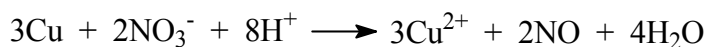
- c. The change in oxidation number can be written as:



To balance for number of electrons lost and gained, multiply the Cu and Cu^{2+} by 3 and the NO_3^- and NO by 2.

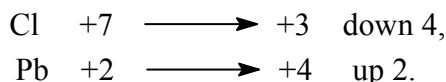


To use up all the O on the left, you need 4 H_2O on the right. This means that there must be 8 H^+ on the left.

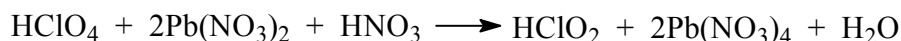


Check: There is a +6 charge on each side.

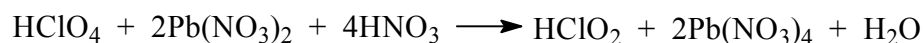
- d. The change in oxidation number can be written as:



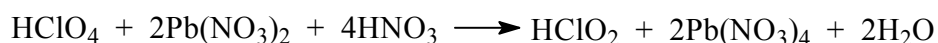
To balance for the number of electrons lost and gained, multiply $\text{Pb}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_4$ by 2.



There are now 5 nitrate groups on the left and 8 on the right. Add 3 more nitrate groups to the left by increasing the HNO_3 to 4 HNO_3 .

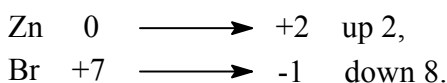


There must be $2\text{H}_2\text{O}$ molecules on the right to balance all the H and O atoms.

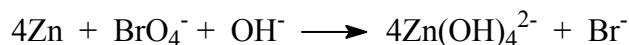


In a molecular equation there is no net charge on either side of the reaction. If you leave the H and O atoms until last to balance them, you will find that you have twice as many H atoms as O atoms left on one side and can make H_2O on the other side. Use this as a check, in other words, if it will not balance for H, O, and H_2O at the end, then you made a mistake somewhere.

e. The change in oxidation number can be written as:



To balance for this change in oxidation number, multiply the Zn terms by 4.



There are now 16 H and 16 O on the right-hand side. This means you need 12 more O (extra to those of the BrO_4^-) and 16 H on the left. The way to do this is to have 8OH^- and $4\text{H}_2\text{O}$ on the left.



Check: There should be a charge of -9 on each side. It is permissible to add water into the equation like this, if necessary. The reactions are occurring in aqueous solution so there is plenty of water around.

Ion-Electron Method

Your textbook provides a thorough description of this second method of balancing redox equations. As outlined there, the process does not take much time once you have had a little practice. In summary, the ion-electron method requires you to:

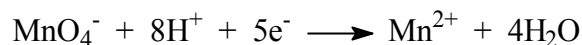
1. Write balanced half-reactions for the oxidation and reduction portions of the reaction.
2. Balance out the oxidation (number of electrons lost) with the reduction (number of electrons gained).

Work through the following problems.

Problem: Balance the equations of the previous problem using the ion-electron method.

Solution:

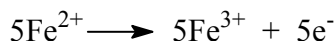
- a. The balanced reduction half-reaction is



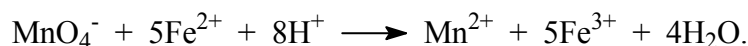
and the balanced oxidation half-reaction is



To balance for the number of electrons gained and lost you have to multiply the oxidation half-reaction by 5.

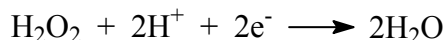


Adding these two half-reactions gives the overall balanced equation



Note that the charge on the left-hand side of this equation is +17 and on the right-hand side is also +17. This is a check that your balanced equation is correct. The charges must also balance.

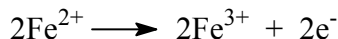
- b. The balanced reduction half-reaction is



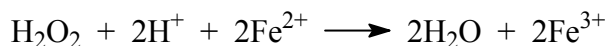
and the balanced oxidation half-reaction is



Now, to balance for the number of electrons lost and gained, you have to multiply the oxidation half-reaction by 2.

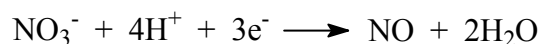


Adding these two half-reactions gives the overall balanced equation



Check: There is a +6 charge on each side.

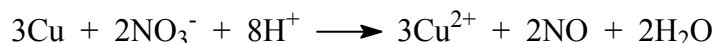
- c. The balanced reduction half-reaction is



and the balanced oxidation half-reaction is

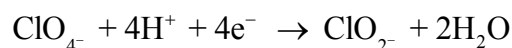


Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2 to balance for electrons lost and gained. This gives the overall balanced reaction as



Note that the charge on each side is +6.

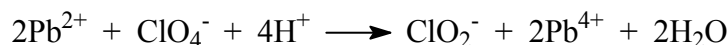
- d. The balanced reduction half-reaction is



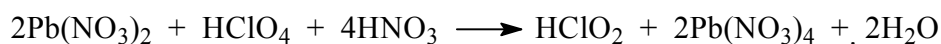
and the balanced oxidation half-reaction is



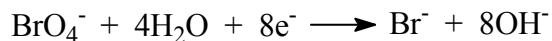
Multiply the oxidation half-reaction by 2 to balance for electrons lost and gained. This gives the overall balanced reaction as



Check: There is a +7 charge on each side. Now put back the “spectator” ions to give the molecular rather than the ionic equation.



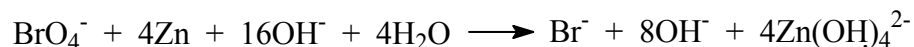
- e. The balanced reduction half-reaction is



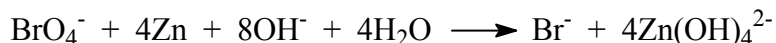
and the balanced oxidation half-reaction is



Multiply the oxidation half-reaction by 4 to balance for electrons lost and gained. The overall reaction equation is



This can be simplified by cancellation of 8 OH⁻ ions on each side.



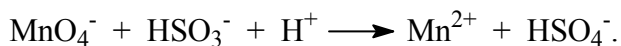
Note that here we used OH⁻ in both the oxidation and reduction half-reactions. (The OH⁻ ions on the right cancel out in the end.) We also added H₂O as necessary. Both of these “tricks” are quite legitimate. The charge on each side of the final equation is -9.

Oxidation-Reduction Titrations

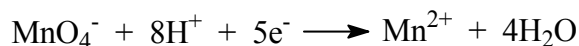
Study Section 4.8 in your textbook. This section describes a practical application of redox equations, the redox titration. You may do a redox titration in the laboratory portion of this course. The important thing to know is how to do redox calculations. These are more complicated than the previous stoichiometric calculations covered in CHEM 1503, since the equation involved is usually more complex. Once you have written a balanced equation, the calculation follows a similar pattern as before. Go over Example 4.13 in the textbook and its practice exercise, and then work through the following problem.

Problem: How many mL of 0.100 M KMnO₄ are needed to oxidize 115 mL of 0.125 M H₂SO₃ if the products include Mn²⁺ and HSO₄⁻?

Solution: The first thing to do in this type of calculation is to write a balanced equation for the reaction. In solution, you have MnO₄⁻ and HSO₃⁻. The unbalanced equation is



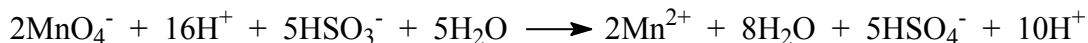
The K⁺ from KMnO₄ is a spectator ion and does not take part in the redox reaction. The balanced reduction half-reaction is



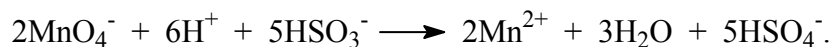
and the balanced oxidation half-reaction is



The reduction half-reaction is multiplied by 2 and the oxidation half-reaction by 5 to give the balanced reaction equation.



This simplifies to



Check: There is a charge of -1 on each side. Now the number of moles of H_2SO_3 present is

$$0.125 \text{ mol L}^{-1} \times 0.115 \text{ L} = 1.44 \times 10^{-2} \text{ moles}$$

From the redox equation stoichiometry, for every mole of H_2SO_3 you need $2/5$ or 0.4 of a mole of KMnO_4 . So the number of moles of KMnO_4 required is

$$0.4 \times 1.44 \times 10^{-2} = 5.76 \times 10^{-3}$$

Using

$$\text{number of moles} = \text{molarity} \times \text{volume},$$

the volume of KMnO_4 required is

$$\frac{\text{number of moles KMnO}_4}{\text{molarity of KMnO}_4 \text{ solution}} = \frac{5.76 \times 10^{-3} \text{ moles}}{0.100 \text{ moles L}^{-1}} = 0.0576 \text{ L}.$$

Thus, 57.6 mL of 0.100 M KMnO_4 are required to oxidize the 115 mL of 0.125 M H_2SO_3 .

Electrochemical Cells

Study Section 18.2 in your textbook. **Galvanic (or voltaic) cells** are electrochemical cells where chemical energy is converted into electrical energy. Any oxidation-reduction equation where ΔG° is negative can, in principle, form the basis of a galvanic cell. However, the practical problems of physically dividing the reaction into oxidation and reduction half-cells prevents this in some cases. Carefully review the operation of the simple galvanic cell discussed here. If you understand the principles of the Cu/Zn cell, you should be able to apply these principles to more complicated galvanic cells. The accepted convention is to draw the **anode** or the **oxidation half-cell** on the left-hand side. The **cathode**, or **reduction half-cell**, is always shown on the right. This means that electrons are always shown as moving from left to right in the external circuit. If you reversed this convention, as shown in Figure 6.1 of this unit, the electrons would move from right to left in the external circuit. In this unit, we will keep to the convention of having the oxidation half-cell on the left-hand side.

A **half-cell** is the cell where a **half-reaction** occurs. There is no such thing as an isolated half-cell, just as there is no such thing as an isolated half-reaction. You can, of course, place a strip of Cu in a solution of Cu^{2+} ions. The reaction



will occur to a very slight degree. Since the electrons generated in this reaction have nowhere to go, a negative electric charge begins to build up in the metal.

This increases the work required to create more Cu^{2+} . The reaction thus comes to an equilibrium when only a minute concentration of Cu^{2+} ions has built up. The concentration of Cu^{2+} is too small to be measured. When an external conductor (a metal wire) and a porous barrier or salt bridge are used to connect the copper half-cell to another half-cell, the circuit is completed. The electrons can move through the external conductor and the reaction “goes.” Until a reaction occurs, the half-cell is not operating as a half-cell. (Of course, that won’t stop us from calling it a half-cell in this unit, since we will assume that we are going to hook it up to another half-cell at some stage!)

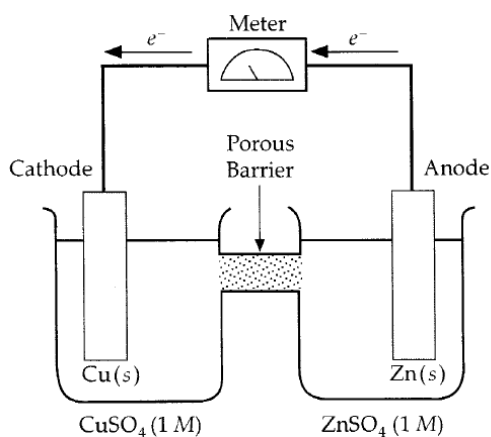


Figure 6.1: The zinc / copper galvanic cell in **reverse convention**.

There are many different types of galvanic cells. The variations are mainly in the types of electrodes and methods of maintaining electrical neutrality. The five most important types of electrodes are:

1. **Metal/metal ion electrode.** These are shown in each half-cell of Figure 18.1 in your textbook.
2. **Gas/ion electrode.** An example of this is the hydrogen electrode serving as the anode in Figure 18.4(b) in your textbook.
3. **Metal/insoluble salt/anion electrode.** An example of this is an electrode consisting of silver and coated with one of its insoluble salts, AgCl . The half-reaction when this electrode acts as a cathode is:

$$\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq).$$
4. **Inert electrode.** An example of this is the strip of platinum shown as the anode in Figure 6.2(d) in this unit. The actual electrode takes no part in the oxidation or reduction. It provides a surface where electrons can be exchanged between the current and the ions involved.

5. **Membrane electrodes.** These are used as one of the electrodes of a pH meter. Their function depends on the fact that a thin glass membrane, separating two solutions of different pH, develops a potential across itself. We will not go into further details about these glass electrodes here. You may have a chance to use one of these in the laboratory portion of this course.

The next problem demonstrates the type of galvanic cell that could be constructed, at least theoretically, from a redox equation.

Problem: Draw a diagram of a galvanic cell based on each of the following redox reactions. Label all the parts of your cell.

- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{H}^+ + 2\text{Cl}^-$
- $2\text{Ag}^+ + \text{Cu}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \text{Cu}^{2+}$
- $2\text{MnO}_4^- + 5\text{Fe}^{2+} + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{Fe}^{3+} + 8\text{H}_2\text{O}$
- $2\text{Fe}^{2+} + \text{Cl}_2(\text{g}) \longrightarrow 2\text{Fe}^{3+} + 2\text{Cl}^-$

Solution: See Figure 6.2 in this unit.

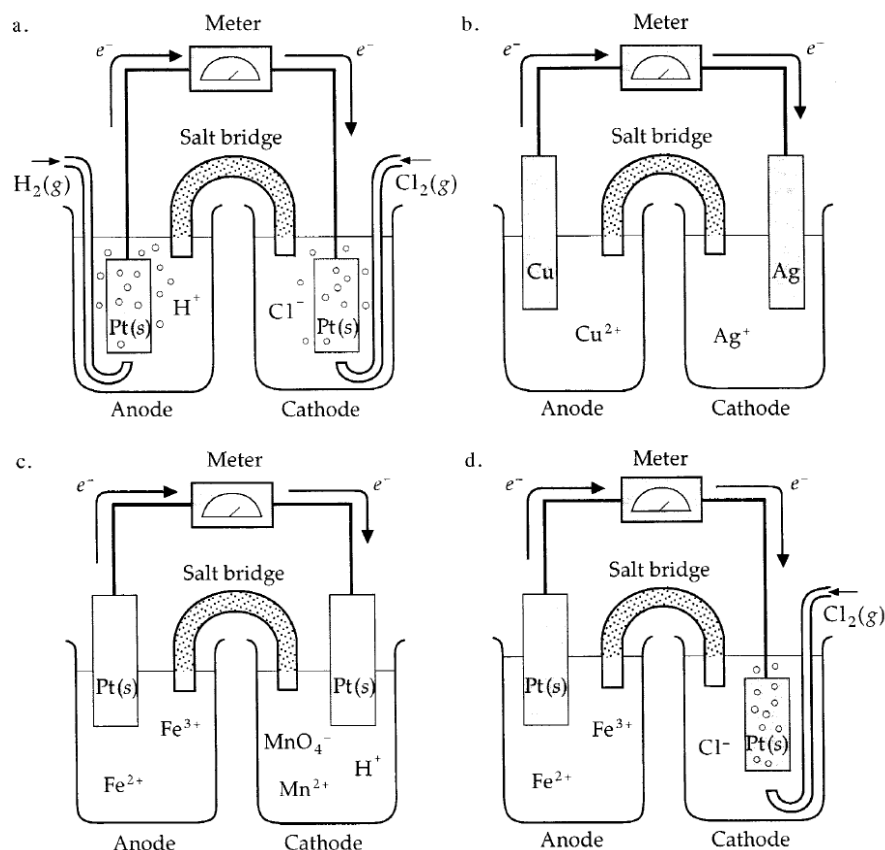


Figure 6.2: Diagrams of galvanic cells.

Problem: Give the cell notation for each galvanic cell in Figure 6.2 in this unit.

Solution:

- $\text{Pt} \mid \text{H}_2 \mid \text{H}^+ \parallel \text{Cl}^- \mid \text{Cl}_2 \mid \text{Pt}$
- $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$
- $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+} \parallel \text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ \mid \text{Pt}$
- $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+} \parallel \text{Cl}^- \mid \text{Cl}_2 \mid \text{Pt}$

In this unit, we have avoided labelling the electrodes as the positive or negative electrode, instead using the terms *anode* and *cathode*. Your textbook also adopts this method. In other chemistry books, you may encounter a sign by the electrode or the words *negative* or *positive* electrode—we have not adopted this system here because it has no real use and can be ambiguous. However, for information purposes (just in case you come across a sign on the electrode in another book or in the laboratory portion of this course), we have included Table 6.1 in this unit. As you can see, the sign of the electrode depends on whether you have an electrolytic or a galvanic cell. But the other conventions remain the same.

Table 6.1: Summary of electrochemical conventions.

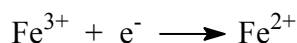
	Cathode	Anode
Direction of e^- flow	into cell	out of cell
Type of ion attracted	cation	anion
Half-reaction	reduction	oxidation
Sign of electrode		
in galvanic cell	positive	negative
in electrolytic cell	negative	positive

Standard Electrode Potential

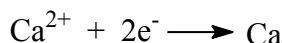
Study Section 18.3 in your textbook. There is no direct way to measure the potential difference between a single electrode and the solution it is in. The potential difference between two electrodes immersed in the same solution is easily measured by placing a voltmeter in the external circuit. The potential difference thus measured is called the **cell potential**. This section of the textbook explains how you can measure the electrode potential *indirectly*. This is done by arbitrarily assigning a zero value to the standard hydrogen electrode. The electrode potential of any other electrode can then be measured when it is connected to this standard.

Table 18.1 of your textbook gives the standard reduction potentials for many electrodes. Take some time to study this table.

You should understand that these values are relative. Hydrogen, assigned a zero value, is around the middle of the table. If the hydrogen half-reaction had been assigned a value of 1.00, then the E° values on the whole table would have been shifted up by 1. The



half-reaction would have an E° value of 1.77 V instead of 0.77 V. The



half-reaction would have an E° value of -1.87 V instead of -2.87 V.

Note that you are not expected to memorize the values in Table 18.1. You can always look them up when you are doing assignments and, in an examination, the appropriate standard reduction potentials or a table of this type would be supplied. You should also note that a table like this is a big help when you are balancing a redox equation, especially if you are using the half-reaction method. Table 18.1 gives balanced half-reaction equations for many of the half-reactions you will encounter. There is nothing wrong with using this to help you balance redox equations. In fact, the more familiar you become with this table, the easier you will find electrochemistry problems.

The following five points, together with the information from your textbook, should help you use Table 18.1 correctly.

1. The E° values are all for standard cells, that is, 1 M solution concentrations and 1 atm pressure for gases. The temperature is 25°C. The next section of this unit explains how to account for non-standard concentrations or pressures.
2. The hydrogen half-reaction is assigned a zero value. Although this assignment is arbitrary, the potential difference between the electrodes at any two electrodes is a directly measurable quantity.
3. All of the half-reactions are written as reductions in Table 18.1 of the textbook. And all of the E° values are for the reduction potential. You may find some chemistry textbooks that also include a table of standard oxidation potentials. To obtain such a table, all you need to do is reverse the half-reaction and the sign of E° . Some examples of standard oxidation potentials are shown in Table 6.2 of this unit. Compare these values to their counterparts in Table 18.1 of the textbook. The relationship is one of reversal. The commonly accepted practice is to use standard reduction potentials. We will keep to this practice in this unit. If you are ever given standard oxidation potentials, it would be a good idea to immediately

write the corresponding reduction equation and reverse the sign of E° . Then, keep to the convention described here. You will find that this means you are less likely to make a mistake. No doubt, you will also find this the easiest system to adopt.

Table 6.2: Standard oxidation potentials at 298 K.

Half-reaction	$E^\circ(\text{V})$
$\text{Li}(s) \rightleftharpoons \text{Li}^+(aq) + e^-$	+ 3.05
$\text{K}(s) \rightleftharpoons \text{K}^+(aq) + e^-$	+ 2.93
$\text{Na}(s) \rightleftharpoons \text{Na}^+(aq) + e^-$	+ 2.71
$\text{Pb}(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2e^-$	+ 0.13
$\text{H}_2(g) \rightleftharpoons 2\text{H}^+(aq) + 2e^-$	0
$\text{H}_2\text{O}_2(aq) \rightleftharpoons \text{O}_2(g) + 2\text{H}^+(aq) + 2e^-$	-0.68
$\text{Fe}^{2+}(aq) \rightleftharpoons \text{Fe}^{3+}(aq) + e^-$	-0.77
$\text{NO}(g) + 2\text{H}_2\text{O} \rightleftharpoons \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^-$	-0.96
$2\text{Cl}^-(aq) \rightleftharpoons \text{Cl}_2(g) + 2e^-$	-1.36
$2\text{F}^-(aq) \rightleftharpoons \text{F}_2(g) + 2e^-$	-2.87

- What does the magnitude of E° mean? *The more positive the E° value, the more it “wants” to reduce.* This last sentence tells you how to use the table. The half-reaction with the more positive E° value will accept the electrons, forcing the other half-reaction to give up electrons (be oxidized). You have to reverse the reaction at the less positive electrode to get the oxidation half-reaction equation.
- You do not change the E° value of the half-reaction under any circumstances. Even if you have to double one half-reaction in order to write a balanced equation, the E° value remains as the value given in Table 19.1 of the textbook. This is where most beginning chemistry students make a mistake, so we will say it another way. *E° values are not affected by the number of electrons in the half-reaction.* If the same reaction is balanced for one electron one time and two electrons another time, E° remains unchanged.

A variation on Table 18.1 of your textbook is given in Figure 6.3 in this unit. In this figure, various redox couples are written with the reduced forms on the left and the oxidized forms on the right.

The oxidized form is an electron-deficient level that can accept an electron and thus act as an electron sink. The zero of the free energy is arbitrarily set at the level of the H_2/H^+ couple, corresponding to the standard E° scale given in Table 18.1. The vertical position of each couple represents the free energy that a mole of electrons would have (in ideal, 1 M solutions) when bound to the electron source.

This concept of electron sources and electron sinks is very similar to that of proton sources and sinks discussed in Unit 4 of this course. There is one major difference between proton-transfer and electron-transfer reactions. Proton-transfer reactions usually take place instantaneously—in less than a millionth of a second. On the other hand, electron transfer reactions can be extremely slow, with the rate affected by the presence of catalysts or the condition of a metal surface. This means that many thermodynamically spontaneous redox reactions may be so slow under most conditions that they can be neglected.

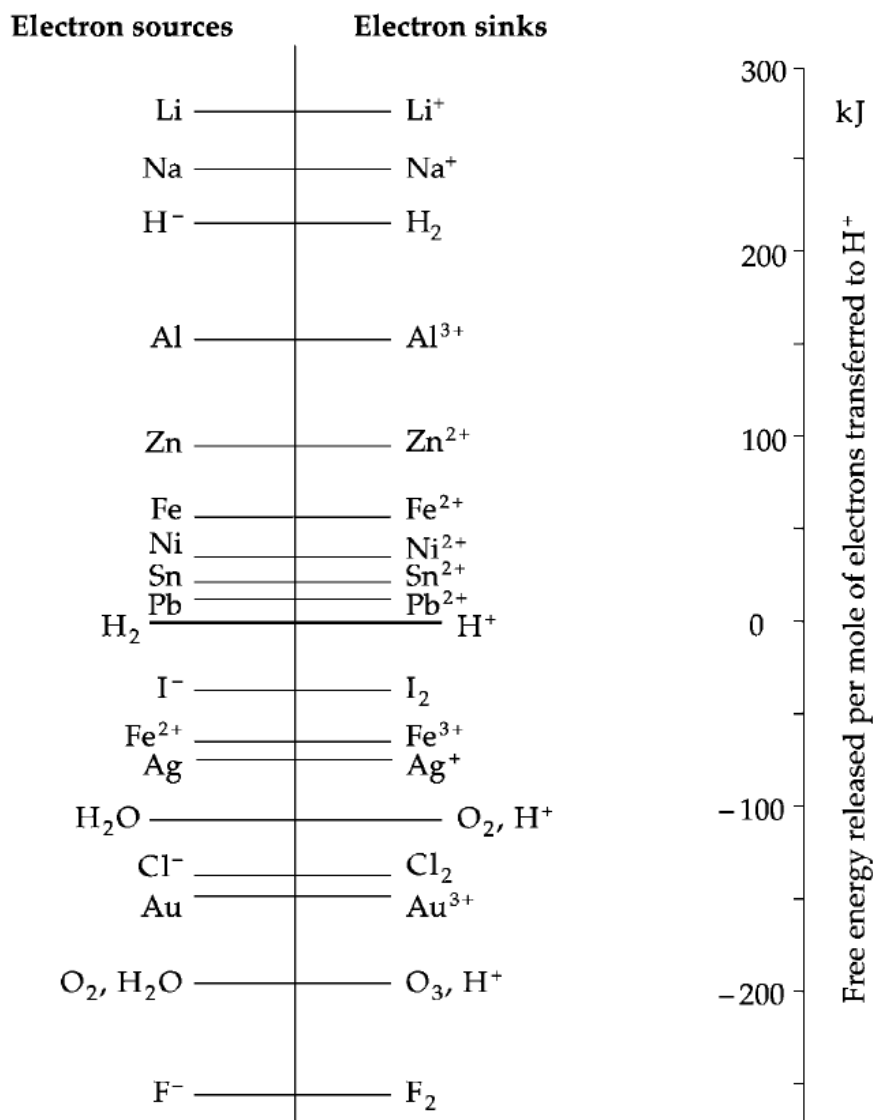
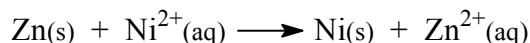


Figure 6.3: Redox couples as electron sources and electron sinks. Electrons will tend to occupy the lowest available free energy level. Chemically, this means that if a piece of zinc metal, for example, is immersed in a solution of NiCl₂, the electron-deficient level of Ni²⁺ can act as a sink to drain off electrons from the Zn above it and to the left. Thus the redox reaction



takes place spontaneously. The fall in free energy is about 50 kJ mol⁻¹. If acid is now added to this solution, the electron sink H⁺ will drain off electrons from the Ni and both metals would be in their oxidized form. Take particular note of the H₂ / H⁺ couple. All metals above this will act as electron sources to the sink H⁺. Any electron sink below the H₂O / O₂, H⁺ couple will drain off electrons from water, oxidizing it to O₂. Chlorine gas, commonly used to disinfect water, will slowly collect electrons and be reduced to Cl⁻.

The standard cell potential can be found using Table 18.1 in the textbook. For a spontaneous equation, that is, an equation that goes from left to right as written, the standard cell potential is found by subtracting the E° value for the oxidizing half-reaction from the reduction E° value:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \text{ or } (E^\circ_{\text{reduction half-reaction}} - E^\circ_{\text{oxidation half-reaction}})$$

This will always give a positive value for E°_{cell} . This is shown for the electrochemical cells in the following problem.

Problem: Write the balanced redox reaction and determine E°_{cell} for the following electrochemical cells.

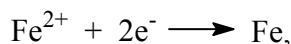
- $\text{Cr} \mid \text{Cr}^{3+} (1 \text{ M}) \parallel \text{Fe}^{2+} (1 \text{ M}) \mid \text{Fe}$
- $\text{Ni} \mid \text{Ni}^{2+} (1 \text{ M}) \parallel \text{NO}_3^- (1 \text{ M}), \text{H}^+ (1 \text{ M}) \mid \text{NO} \mid \text{Pt}$
- $\text{Ag} \mid \text{Ag}^+ (1 \text{ M}) \parallel \text{MnO}_4^- (1 \text{ M}), \text{H}^+ (1 \text{ M}), \text{Mn}^{2+} (1 \text{ M}) \mid \text{Pt}$
- $\text{Pt} \mid \text{Cr}_2\text{O}_7^{2-} (1 \text{ M}), \text{H}^+ (1 \text{ M}), \text{Cr}^{3+} (1 \text{ M}) \parallel \text{Al}^{3+} (1 \text{ M}) \mid \text{Al}$

Solution:

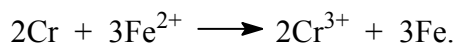
- In the cell notation the oxidation (anode) half-cell is always on the left. Thus, the oxidation half-reaction is



the reduction half-reaction is



and the overall balanced equation is



Using the standard reduction potentials from Table 19.1 in the textbook and

$$(E^\circ_{\text{reduction half-reaction}} - E^\circ_{\text{oxidation half-reaction}}),$$

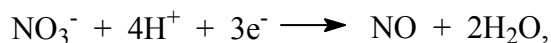
that is, difference in reduction potentials,

$$E^\circ_{\text{cell}} = (-0.44 \text{ V}) - (-0.74 \text{ V}) = 0.30 \text{ V}$$

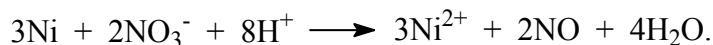
- b. The oxidation half-reaction is



the reduction half-cell is



and the overall balanced redox reaction is



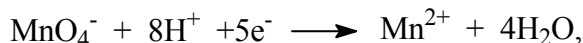
From Table 18.1 in the textbook,

$$E^{\circ}_{\text{cell}} = (0.96 \text{ V}) - (-0.25 \text{ V}) = 1.21 \text{ V}$$

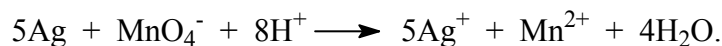
- c. The oxidation half-reaction is



the reduction half-cell is



and the overall balanced redox reaction is



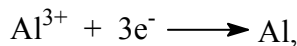
From Table 18.1 in the textbook,

$$E^{\circ}_{\text{cell}} = (1.51 \text{ V}) - (0.80 \text{ V}) = 0.71 \text{ V}$$

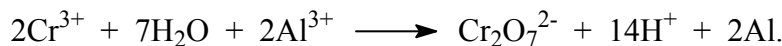
- d. The oxidation half-reaction is



the reduction half-cell is



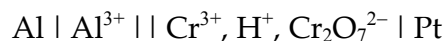
and the overall balanced redox reaction is



From Table 19.1 in the textbook,

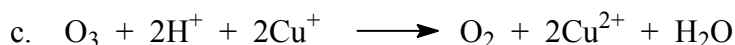
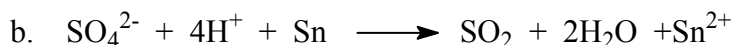
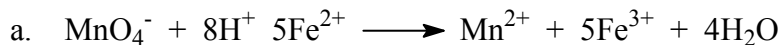
$$E^{\circ}_{\text{cell}} = (-1.66 \text{ V}) - (1.33 \text{ V}) = -2.99 \text{ V}$$

Something is wrong! A negative value for E°_{cell} means that the reaction is not spontaneous as written. The reaction is spontaneous in the *reverse* direction to that in the equation above, and the cell notation for the galvanic cell should have been



Any spontaneous oxidation-reduction reaction can, at least theoretically, become the basis for a galvanic cell. As mentioned before, not all such reactions give practical cells but it is a good exercise to devise such cells.

Problem: Give the cell diagram notation and determine E°_{cell} for the galvanic cell that could be constructed from the following redox reactions.

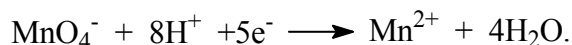


Solution:

- a. The oxidation half-reaction here is



and the reduction half-reaction is



The cell notation (oxidation half-cell on the left) is



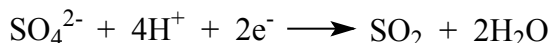
From Table 18.1 in the textbook,

$$E^\circ_{\text{cell}} = (1.51 \text{ V}) - (0.77 \text{ V}) = 0.74 \text{ V}$$

- b. The oxidation half-reaction here is



and the reduction half-reaction is



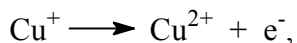
The cell notation (oxidation half-cell on the left) is



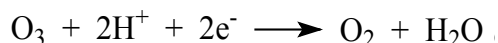
From Table 18.1 in the textbook,

$$E^\circ_{\text{cell}} = (0.20 \text{ V}) - (-0.14 \text{ V}) = 0.34 \text{ V}$$

- c. The oxidation half-reaction here is



and the reduction half-reaction is



The cell notation (oxidation half-cell on the left) is

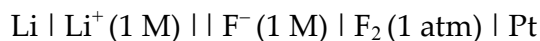


From Table 18.1 in the textbook,

$$E^\circ_{\text{cell}} = (2.07 \text{ V}) - (0.15 \text{ V}) = 1.92 \text{ V}$$

Problem: Use the standard reduction potentials given in Table 18.1 of the textbook to devise the galvanic cell with the greatest E°_{cell} . What would be the practical difficulties encountered in constructing such a cell?

Solution: The greatest cell potential would be obtained using half-cells with the greatest difference in standard reduction potential. Using the standard reduction potentials in Table 18.1 from the textbook, the cell



would have an E°_{cell} of $(2.87 \text{ V}) - (-3.05 \text{ V}) = 5.92 \text{ V}$. However, Li is an extremely reactive metal and would react with the water in the half-cell. The difficulty with a fluorine half-cell is that fluorine is an extremely corrosive gas and fluorine itself would oxidize water. Practically, it is better to have a lower E°_{cell} and safer electrodes.

Now work through Examples 18.2 and 18.3 in your textbook and their practice exercises.

Spontaneity of Redox Reactions

Study Section 18.4 in your textbook. The equation

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

gives a method of relating thermodynamics to electrochemistry. The symbol n represents the number of moles of electrons transferred in the balanced redox reaction. If you had to balance the equation to begin with, then you would know what n is. But if you were given the equation as balanced, then you would have to break it down into the oxidation and reduction components in order to find n . Once you have had a bit of practice, you may be able to determine the value of n just by looking at the change in the oxidation number of either participant. In Unit 5 of this course, you related thermodynamics to equilibrium constants in

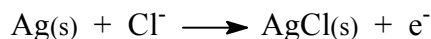
$$\Delta G^\circ = -RT \ln K$$

Combining these two equations gives

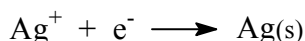
$$-nFE^\circ = -RT \ln K \quad \text{or} \quad nFE^\circ = RT \ln K$$

$K > 1$ means the equation equilibrium lies to the right. $\ln K$ will be a positive value. This in turn means that E° will be positive for a galvanic cell based on the equation. This is explained well in your textbook. Spend as much time as you need to grasp this as it is important that you understand the meaning of E° as explained in your textbook. Go over Examples 18.4 and 18.5, and their practice exercises, to help you clarify the relationship between equilibrium (K) and electrochemistry (ΔG°). With a very large value of K , it would be impossible to measure its value with any degree of accuracy using the “concentration of products over concentration of reactants method.” But its corresponding E° value can be measured accurately. Thus, electrochemistry provides a simple method of measuring very large (or very small) equilibrium constants. In Unit 3 of this course, you may have wondered how those very small values of solubility product were measured. K_{sp} for CuS is 5.9×10^{-37} . So, the solubility of CuS is $7.7 \times 10^{-19} \text{ mol L}^{-1}$ or $7.4 \times 10^{-17} \text{ g L}^{-1}$. It is obvious that $7.4 \times 10^{-17} \text{ g}$ could not be weighed accurately to make this measurement. If you scaled this weight up to a value that could be measured (for example, 0.0074 g), you would have to dissolve it in 10^{14} litres of liquid—again, extremely impractical. The following problem illustrates the elegant solution to perplexities of this sort.

Problem: The standard cell potential for the electrochemical cell with oxidation half-reaction

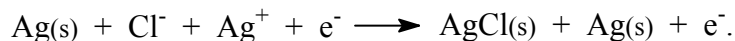


and reduction half-reaction

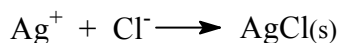


is 0.58 volts. Calculate K_{sp} for AgCl from this data (assume a temperature of 25°C).

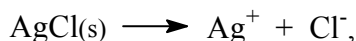
Solution: The overall cell reaction is



This reduces to



with an E° value of 0.58 volts. For the reverse of this equation,



The E° value is -0.58 volts. Of course, this last equation is that for the dissolution of the sparingly soluble salt, AgCl. The K value for this reaction is its K_{sp} . Using

$$nFE^\circ = RT \ln K$$

we find that

$$\begin{aligned}\ln K &= \frac{nFE^\circ}{RT} \\ &= \frac{1 \times 96500 \text{ C mol}^{-1} \times (-0.58 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = -22.6\end{aligned}$$

and

$$K = 1.5 \times 10^{-10}$$

The K_{sp} value quoted for AgCl in Table 16.2 of your textbook is 1.6×10^{-10} . Note that in the above calculation the units J, C, and V cancelled. One joule is one coulomb-volt. It is worthwhile making a note of this relationship somewhere in your notes. It is also given inside the back cover of your textbook.

Non-Standard Galvanic Cells

Study Section 18.5 in your textbook. The **Nernst equation**,

$$E = E^\circ - \frac{RT}{nF} \ln Q,$$

usually written for 298 K as

$$E = E^\circ - \frac{0.0257}{n} \ln Q,$$

is used to account for difference in potential in non-standard cells. You have already encountered Q , the equilibrium or reaction quotient, in Unit 3 of this course. It has the same form as K , the equilibrium constant. You have to be able to deduce the value of n , the number of moles of electrons transferred in the reaction. This means splitting a given redox equation into reduction and oxidation half-reactions.

At equilibrium, no further reaction takes place—there is no more transfer of electrons. No current flows, E°_{cell} is zero, and $Q = K$. Thus

$$0 = E^\circ - \frac{0.0257}{n} \ln K$$

or

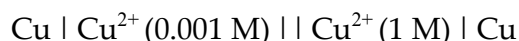
$$\ln K = \frac{nE^\circ}{0.0257}$$

This is a useful relationship between the equilibrium constant and the standard cell potential, as you saw in the previous section.

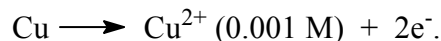
The use of the Nernst equation is demonstrated in Examples 18.6 and 18.7 in your textbook and their practice exercises. Work carefully through these examples. Note that Example 18.7 could be the basis for a pH meter; however, the pH meters you might use in the laboratory are not the same as the standard hydrogen electrode.

Concentration Cells

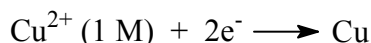
Concentration cells are constructed from two half-cells with the same electrode reaction, but differing concentrations or gas pressures. For example, consider the voltaic cell



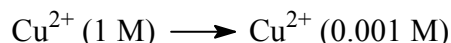
There is a potential difference between the two electrodes due to a difference in concentration. The oxidation half-reaction is



At the anode, Cu gives up electrons and forms Cu^{2+} ions. This means the concentration of Cu^{2+} ions increases in the oxidation half-cell. At the cathode, the reduction reaction



means that the concentration of Cu^{2+} ions decreases from the initial 1 M value. Overall, the reaction can be written as



meaning that the concentration decreases at the more concentrated electrode and increases at the more dilute electrode. Eventually both concentrations will be the same, no further reaction will occur, no electrons will transfer, and the cell will have “run down.” This is what you would expect to happen for a spontaneous reaction. You should not expect the more concentrated solution to become even more concentrated and the dilute solution even more dilute. It would be a contravention of the second law of thermodynamics. The driving force behind a concentration cell is the entropy increase obtained when the concentrations even out. The reaction in a concentration cell has a negative ΔG , but in this case the free energy change is totally due to an entropy increase. For this concentration cell,

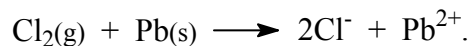
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257}{n} \ln Q$$

However, in a concentration cell $E^\circ = 0$ (the standard reduction potential is the same for both sides), E depends only on the concentration correction term $0.0257/n \times \ln Q$. So,

$$\begin{aligned} E_{\text{cell}} &= 0 - \frac{0.0257}{2} \times \ln \frac{0.001}{1} \\ &= -0.0129 \times \ln 0.001 \\ &= 0.0891 \text{ V.} \end{aligned}$$

Mathematically, for the value of E to be positive in a concentration cell, the Q ratio must be less than 1. This means that $\ln Q$ will be a negative number. Then the two negative terms multiplied together give a positive value for E —a spontaneous reaction.

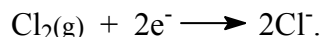
The Nernst equation can be used to demonstrate why the potential of a half-reaction is not related to the coefficients in the equation. Consider the reaction



If the gas is at 1.5 atm pressure and all the ionic concentrations are 0.1 M, you can calculate E_{cell} using the Nernst equation. The oxidation half-reaction is



and the reduction half-reaction is



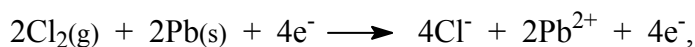
Using the data in Table 18.1,

$$E^\circ_{\text{cell}} = +1.36 \text{ V} - (-0.13 \text{ V}) = 1.49 \text{ V}$$

From the half-reactions you can see that n is 2. Thus, in the Nernst equation,

$$\begin{aligned} E_{\text{cell}} &= E^\circ - \frac{0.0257}{n} \times \ln \frac{[\text{Cl}^-]^2 [\text{Pb}^{2+}]}{p_{\text{Cl}_2}} \\ &= 1.49 - \frac{0.0257}{2} \times \ln \frac{(0.1)^2 (0.1)}{1.5} \\ &= 1.49 - \frac{0.0257}{2} \times \ln (6.67 \times 10^{-4}) \\ &= 1.49 - \frac{0.0257}{2} \times (-7.31). \quad (1) \end{aligned}$$

We will leave this calculation at point (1) above, so that we can compare it to the result you would obtain if the original equation was written as doubled; that is,



This is chemically the same as the original equation. Doubling the coefficients does not change the chemical reaction. The value for the cell potential is calculated as

$$\begin{aligned} E_{\text{cell}} &= 1.49 - \frac{0.0257}{4} \times \ln \frac{(0.1)^4 (0.1)^2}{(1.5)^2} \\ &= 1.49 - \frac{0.0257}{4} \times \ln (6.67 \times 10^{-4})^2 \\ &= 1.49 - \frac{0.0257}{4} \times 2(-7.31). \end{aligned} \quad (2)$$

Calculation of (2) above gives the same calculation as (1). If you double the coefficients, you double the value of n . Also, the value of Q is squared. $\ln Q$ is thus doubled and this cancels with the doubled value of n . This demonstrates that cell potential is not related to the coefficients of the equation. This is different from ΔG and K values that do depend on whether the equation is written as doubled, tripled, and so on (see Units 3 and 5 of this course).

Applications of Electrochemistry

Study Sections 18.6 and 18.7 in your textbook. You do not have to memorize the details of various batteries or of methods of dealing with corrosion, but you should be able to apply the principles you have studied to these examples of electrochemical reactions.

Batteries and Fuel Cells

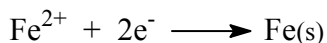
A good definition of a **battery** is a galvanic cell that has practical applications. Batteries are energy storage devices and are often used commercially. Some galvanic cells may be too expensive, too corrosive, or have too high an internal resistance to be commercially viable. The galvanic cell or cells of batteries are capable of supplying a comparatively large current—at least for a short period of time. The term *battery* originally meant two or more galvanic cells connected in series to produce a voltage equal to a multiple of the single cell voltage. Nowadays, the word is used to mean one or more cells. Recent advances in battery technology are described in your textbook. Make sure you understand the overall electrochemical reaction (and its component anode and cathode reaction) of the dry-cell battery, the mercury battery, the lead storage battery, and the solid-state lithium battery, but note that you do not have to memorize these reactions.

Fuel cells are distinguished from batteries in that they do not store chemical energy within the cell. The anode and cathode materials are continuously replaced as they are used up in the production of an electrical current. Your textbook describes the hydrogen-oxygen fuel cell. The advantages of fuel cells, in comparison to heat engines, include minimal number of moving parts to go wrong, 60 to 80% efficiency as opposed to 30 to 40%, and virtually zero air pollution. The disadvantage of fuel cells is that they require a cathode material where the reduction of oxygen occurs rapidly. This reaction, although thermodynamically spontaneous, happens to be very slow. The best cathode materials so far discovered are expensive metals such as platinum. Therefore, the high cost of fuel cells has, unfortunately, limited their applications. The development of fuel cells continues to be an area of great research interest.

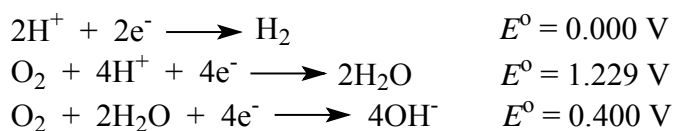
You may remember that the Apollo 13 mission had to be aborted before the moon landing, due to an explosion in an oxygen storage tank. The oxygen was not only the life support for the Apollo 13 crew but also one of the fuels for the hydrogen-oxygen fuel cell. This meant that the astronauts had to shut down all but the most essential electrical systems to maintain enough power to make necessary navigational manoeuvres and use the Lunar Excursion Module for life support. Despite problems such as this (luckily very rare), a hydrogen-oxygen fuel cell is an ideal electrical generator for manned space flight. The only by-product of the reaction is water, another essential life-support requirement

Corrosion

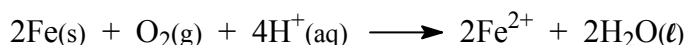
The corrosion of iron is a serious economic problem and the cost of replacing rusted iron objects is billions of dollars a year. The corrosion mechanism is basically that of a galvanic cell. The half-reaction



has a standard reduction potential of -0.44 V (from Table 18.1 in your textbook). This standard reduction potential is less positive than any of the following half-reactions.



Thus, the $\text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}$ reaction is less likely to reduce. In fact, it is reversed and the iron is oxidized to Fe^{2+} . In the presence of water and oxygen the rusting of iron is spontaneous. An overall equation for the rusting process in acid solution can be written as



or in neutral solution as



Iron(II) hydroxide is then ordinarily further oxidized.

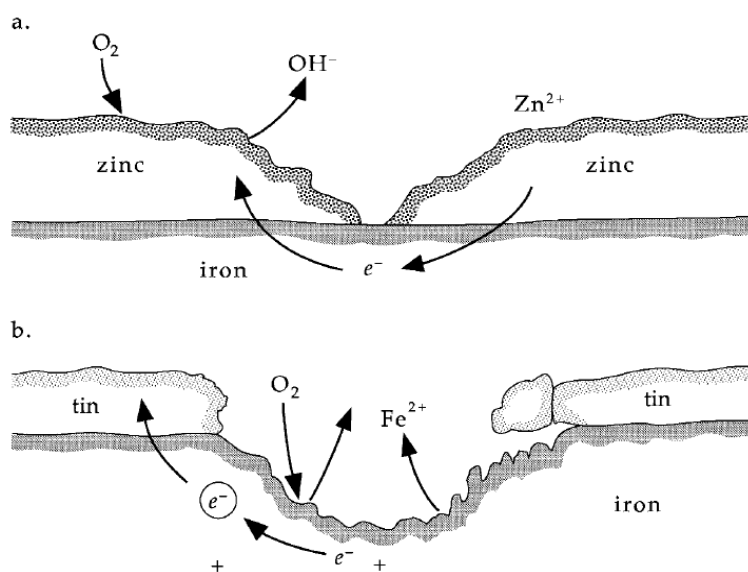
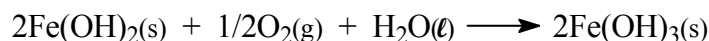


Figure 6.4: Corrosion prevention by metal coating. **a.** Sacrificial coating; **b.** Noble coating.

Refer to Figure 6.4(a) above. In galvanized steel, a coating of Zn is placed on the Fe. Zn is a better electron donor than Fe. This means that Fe^{2+} ions will act as electron sinks to Zn and be reduced back to Fe. Thus, when a scratch develops on a galvanized surface, an electro-chemical cell is formed. This cell injects a few electrons into the Fe, making it slightly negative and less likely to dissolve in Fe^{2+} ions. This is a form of cathodic protection, where the Zn acts as a **sacrificial coating**. What little Fe^{2+} is formed gets turned back into Fe at the expense of Zn. Figure 6.4(b) shows how tin is used as a **noble coating** to prevent corrosion in tin cans. Sn occurs below the H_2/H^+ couple in the electromotive series, so, unlike Fe (in steel), it will not react with the (organic) acids found in most vegetables and fruit. Tin plating is purely protective. Once a scratch or a pinhole develops, moisture gets in and corrosion quickly follows. The moisture allows an electrochemical cell where Fe is spontaneously oxidized to Fe^{2+} as electrons drain away to Sn^{2+} . (The Sn/Sn^{2+} couple is below the Fe/Fe^{2+} couple.)

The final product, a flaky, loose, reddish-brown deposit (rust) has the characteristic colour of iron(III) hydroxide. The actual chemical composition of rust is more complicated than this. Your textbook describes it as $\text{Fe}_2\text{O}_3 \cdot (x\text{H}_2\text{O})$.

The essence of electrochemical corrosion is the removal of electrons from a metal. There are three common electron sinks that are important in this regard. These are hydrogen ions (only for some metals), oxygen (for all but a few metals), and any “less active” metal. You should be able to relate this to Figure 6.3 in this unit. A particularly insidious feature of corrosion is that the site of the metal dissolution can be considerably removed from where the oxygen or hydrogen ions are withdrawing electrons. You may have noticed corrosion spreading under a scratch or pinhole in the paintwork of a car. The iron actually dissolves more readily under the more protected areas still covered by paint. Merely covering it up with more paint will not help if the electrons are traveling through the metal to some other site where they are being picked up by O_2 .

Rusting occurs at a much lower rate in desert areas where the water vapour content of the air is very low. Near the ocean, or in areas where salt is used on winter roads, corrosion occurs at a faster rate. The droplets of water on the metal contain dissolved salts and are thus more effective electrolytic solutions for conducting electricity. Prevention of corrosion concentrates on keeping water and oxygen away from the metal surface—methods for doing this are discussed in your textbook. Figure 6.4 in this unit diagrams sacrificial and protective coating as means of preventing or, more realistically, delaying, corrosion.

Biological Oxidation

The electron-transfer processes occurring in biological systems are more complicated than the simple systems we have dealt with so far in this unit. However, the principles involved are the same. Oxidation-reduction reactions are an extremely important type of metabolic process. A complex series of steps involving successive electron transfers account for the utilization of molecular oxygen in the controlled “combustion” of food. Many of the steps also involve proton transfer, and all are catalyzed by enzymes. Your textbook does not address biological oxidation but, since many students are interested in biology, this unit covers some aspects of biological oxidation. You do not need to learn the biological terms or details, but you should be able to relate this to electrochemical principles.

If you have taken biology courses, you have probably encountered the series of reactions, known as **glycolysis**, responsible for the stepwise metabolism of sugars. The **tricarboxylic acid cycle** (or **citric acid cycle**, or **Krebs cycle**) is the next series of metabolic reactions. Eventually, electrons from the tricarboxylic acid cycle enter the electron-transport chain (electron-transfer chain). This series of reactions collects the electrons released at various prior metabolic stages and passes them through successive oxidation-reduction steps. This is possible because carbohydrate is high up on the electron source / electron sink chart, whereas oxygen is very low.

In other words, oxygen serves as an electron sink for any carbon compound containing hydrogen. During the electron-transport process, released energy is incorporated into ATP (adenosine triphosphate). This substance later releases stored energy at other sites in the organism, where it is available for anabolic (building up) reactions. A summary of the major components of this chain is shown in Figure 6.5 of this unit. Note that the reduction potential of each successive half-reaction is greater than the one above. Thus, the spontaneous direction of electron flow is from the reduced metabolic substances to oxygen. The uptake of O_2 has the highest standard reduction potential of all the half-reactions in the chain. It is the last reaction of the series.

Destruction or inhibition of any of the enzymes that catalyze these oxidation-reduction reactions prevents the passage of the electrons and ultimately the uptake of respiratory oxygen. The cyanide ion (CN^-) forms a complex with cytochrome $a-a_3$, preventing its interaction with oxygen. This is a rapid and non-reversible reaction and accounts for the rapid effect of cyanide poisoning. The victim asphyxiates, not from a lack of oxygen, but from an inability to use that oxygen. Examples of other substances that affect enzymes of the electron-transport system are the fish poison rotenone, barbiturates, and certain antibiotics such as antimycin A. In large enough doses these substances can prove fatal in humans.

In anaerobic respiration the electron sink is much higher in energy than oxygen. Far less free energy is liberated when carbohydrate is anaerobically oxidized to methane or alcohol. Thus, fermentation is a much less efficient process than aerobic respiration.

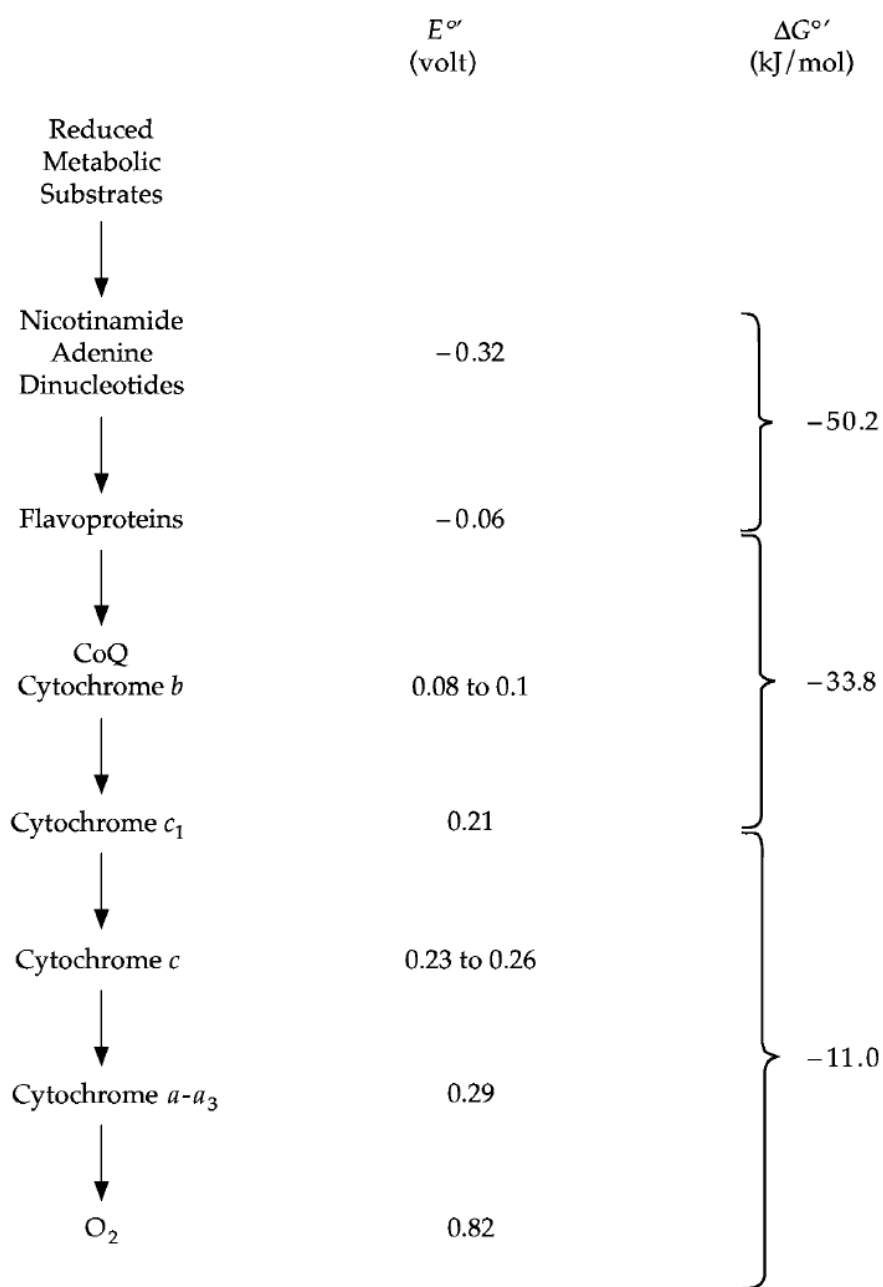


Figure 6.5: A simplified version of the mitochondrial electron-transport chain. The superscript (') in $E^{\circ'}$ and $\Delta G^{\circ'}$ indicates 25°C and pH 7. The values are approximate.

Electrolysis

Study Section 18.8 in your textbook. **Electrolysis** is a process where an otherwise non-spontaneous reaction ($\Delta G > 0$) is forced to take place by the application of energy from an outside source. The free energy required to force the reaction to go in the desired direction is furnished by the electrical energy supplied to the cell.

You should know the meaning of the following terms, many of which have already appeared in this unit.

Electrochemical cell: A device that permits the interconversion of chemical and electrical energy. An electrochemical cell can, in principle, be operated in either of two directions. In one direction the cell is called electrolytic and in the other, galvanic.

Electrolytic cell: A cell in which electrical energy is converted to chemical energy. The cell reaction is made to run “uphill,” yielding products with free energy that is higher than that of the reactants. A cell operated in this direction is an energy consumer. This is the type of cell discussed in Section 18.8 in your textbook. Figures 18.17 and 18.19 are examples of electrolytic cells. Another definition of an electrolytic cell is one in which electrolysis occurs.

Galvanic (or voltaic) cell: A cell in which chemical energy is converted to electrical energy. In a cell run in this direction the cell reaction takes place spontaneously, leading to products having a lower free energy than the reactants. Such a cell is an energy producer. This type of electrochemical cell is discussed in Section 18.2 of your textbook.

Electrodes: Devices that allow electrons to enter and leave electrochemical cells. Electrodes provide surfaces where the oxidation and reduction half-reactions can occur. Often electrodes are made of inert materials, but they can also take part in the electrochemical reaction. Electrodes are either anodes or cathodes.

Anode: The electrode where oxidation occurs (electrons flow away from the anode).

Cathode: The electrode where reduction occurs (electrons flow towards the cathode).

(A simple way to remember the difference between these is the mnemonic “polecat”: ***P**ositive ions **l**eave the solution at the **c**athode*. Positive ions leave the solution in order to collect electrons. They pick up these electrons—reduction—at the cathode. So if you remember the word *polecat*, you can always work out that reduction occurs at the cathode. You can also use “polecat” to determine the direction that ions move in the solution being electrolyzed.)

Current: A flow of electrons. Currents are measured in amperes (or amps). The ampere (A) is a basic SI unit. If a current of 1 amp (A) flows for 1 second (s), the total charge supplied is 1 coulomb (C).

$$C = A s$$

One mole of electrons has a total charge of 9.65×10^4 coulombs.

The movement of ions constitutes the current within an electrolytic cell. The electrodes themselves become the electron donors and acceptors when a potential difference is applied across them. The cathode delivers electrons to nearby positive ions, while the anode accepts electrons from negative ions near that electrode. As the reacting ions are consumed near the two electrodes, more ions diffuse into these regions to take their place. This means electrolysis can occur with molten salts or with aqueous solutions of ionic species—in both cases the ions are free to move. Your textbook describes examples of this.

The electrolysis of molten NaCl is shown in Figure 18.17(a) of your textbook. At high temperatures, solid sodium chloride melts. The kinetic energy supplied allows the Na^+ and Cl^- ions to overcome the attractive forces holding them in the lattice of a solid. These ions are then free to move in the molten salt. Note that when an electric current is applied, the cations (Na^+) move toward the cathode. There they accept an electron and are deposited on the cathode as sodium metal. Chloride ions move towards the anode. There they lose an electron (oxidation) and become elemental chlorine. Chlorine gas, Cl_2 , bubbles off the molten salt around the anode region. This process continues as long as the electric current is supplied. Left to itself, molten sodium chloride remains as sodium chloride. The decomposition to elements is not a spontaneous reaction.

Aqueous solutions of ionic species contain mobile charged species and can thus undergo electrolysis. In the case of aqueous sodium chloride, the products are chlorine gas and hydrogen gas. The electrolysis of pure water proceeds extremely slowly since there are relatively few H^+ or OH^- ions to carry the electric current. The addition of electrolytes, such as H_2SO_4 , provides ions to carry the current, but the net result is still considered as the electrolysis of water. The products are hydrogen and oxygen gas.

Another application of electrolysis is found in the electroplating industry. The metallic object to be plated is used as the cathode in a solution of the appropriate ion. Metals such as silver, gold, copper, and chromium electroplate out as a thin even coating over the cathode.

Faraday's Laws

The stoichiometric relationships between chemical reactions and electrical energy are summarized in **Faraday's laws**, given below.

1. The mass of a substance formed or consumed in an electrolysis is proportional to the amount of charge passing through it.
2. The mass of a substance formed or consumed in an electrolysis is also proportional to its molar mass.
3. The mass of a substance formed or liberated in an electrolysis is inversely proportional to the number of electrons per mole needed to cause the indicated change in oxidation state.

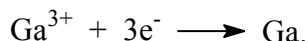
To do calculations involving Faraday's laws (and all electrolysis calculations are based on Faraday's laws) you use the following pieces of information:

- a. A balanced half reaction
- b. The charge of one mole of electrons is 9.65×10^4 coulombs
- c. One coulomb (charge) = one amp (current) \times one second (time)

Notice that it is not always necessary to write a balanced full redox reaction for these problems. You are sometimes asked to calculate the quantities produced at the anode and at the cathode. As long as you have balanced half-reactions for each electrode you can do the calculation, but then, if you have balanced half-reactions, it only takes a further small effort to write a balanced overall redox reaction. Try Example 18.8 in the textbook and its practice exercise, and then work through the problems below.

Problem: How many coulombs of electricity are needed to plate out 27.5 g of gallium from a solution of $\text{Ga}_2(\text{SO}_4)_3$?

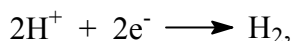
Solution: The balanced reduction half-reaction responsible for plating out gallium is



So, 3 moles of electrons are needed to plate out 1 mole (69.7 g) of gallium. Note that 27.5 g of gallium will need $3 \times 27.5 \text{ g} / 69.7 \text{ g} = 1.18$ moles of electrons. One mole of electrons is 1 faraday = 96 600 C, so 1.18 moles of electrons is $1.18 \times 96\,500 = 1.14 \times 10^5 \text{ C}$.

Problem: A solution of H_2SO_4 is electrolyzed between inert electrodes. Formed at the cathode during 40 minutes of electrolysis are 325 mL of H_2 gas at 720 mm Hg and 28°C . How many mL of oxygen gas, collected under the same conditions, are formed at the anode during this time?

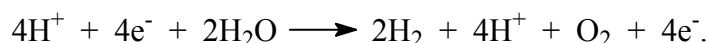
Solution: The problem is most easily solved by considering the balanced equation for the electrolysis reaction. The reduction half-reaction is



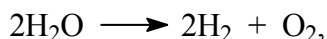
the oxidation half-reaction is



and the overall balanced equation is



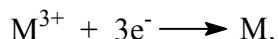
This reduces to the electrolytic decomposition of water,



where twice as many moles of hydrogen gas are produced as oxygen gas. From the gas laws in Unit 1 of this course, you know that equal numbers of moles of different gases occupy the same volumes under the same conditions. Therefore, the oxygen gas in this electrolysis will occupy half the volume of hydrogen, that is, $325 \div 2 = 162.5$ mL.

Problem: A metal forms the chloride MCl_3 . If a current of 3.86 A is passed through the molten chloride for 20.7 minutes, 1.60 g of the metal, M, is deposited at the cathode. What is the atomic mass of the metal?

Solution: The cathode reaction is



Thus, 1 mole of M^{3+} ions requires 3 moles of electrons to deposit 1 mole of M atoms (atomic mass). Using

$$C = A \times \text{time},$$

charge available = $3.86 \text{ A} \times 20.7 \text{ min} \times 60 \text{ s min}^{-1} = 4.79 \times 10^3 \text{ C}$. $4.79 \times 10^3 \text{ C}$ deposits 1.60 g of M at the cathode. So, $3 \times 96\,500 \text{ C}$ (3 moles of e^-) deposits the atomic mass of M.

$$\text{atomic mass of M} = 1.60 \text{ g} \times \frac{3 \times 96,500 \text{ C}}{4.79 \times 10^3 \text{ C}} = 96.6 \text{ g}$$

Use the summary at the end of Chapter 18 of your textbook to review the important concepts of electrochemistry.

Self-Assessment

Having reached the end of Unit 6, you should be able to:

- Balance oxidation-reduction equations.
- Write the oxidation and the reduction half-reactions for any redox equation.
- Perform calculations from redox titrations.
- Draw a cell diagram or a cell notation for the electrochemical cell based on a given redox equation.
- Deduce standard cell potentials from tables of standard reduction potentials.
- Calculate non-standard cell potentials using the Nernst equation.
- Calculate ΔG and K values from the appropriate electrochemical data.
- Calculate cell potentials for concentration cells.
- Do Faraday's law calculations.

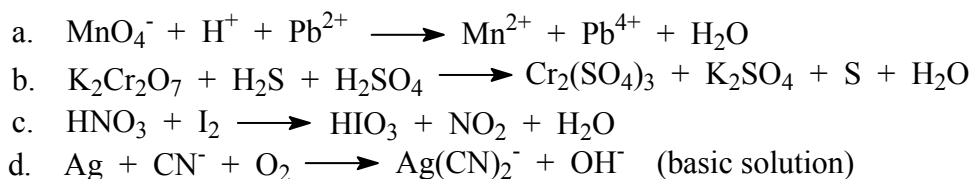
Practice Exercise 6

Finish working through Unit 6 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise. You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 6. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 6 section of the Course Units.

1. In each of the following give the oxidation number of
 - a. The chlorine atom in: Cl_2O , ClO_3^- , HCl , Cl_2O_7
 - b. The phosphorus atom in: H_3PO_4 , P_4O_6 , P_4O_{10}
 - c. The uranium atom in: UF_6 , UO_2^{2+} , UCl_3 , UO_3
 - d. The nitrogen atom in: NH_3 , N_2O , H_2NNH_2 , NO_3^- , N_2O_4

2. Balance the following redox equations using either the oxidation number change method or the ion-electron method.



3. From the following electrolysis data, calculate the charge on the electron, expressed in coulombs.

A current of 0.61 A was passed through a 3.0 M solution of H_2SO_4 for 60.0 minutes. The evolved hydrogen gas, H_2 , was collected over water and was found to occupy a volume of 288 mL at 27°C and total pressure of 767 torr. You will also need the following values.

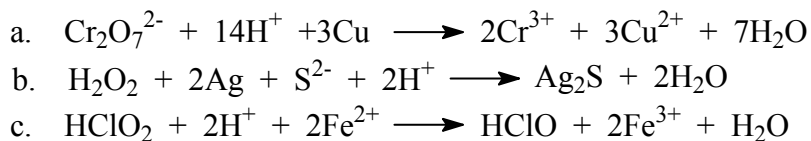
Avogadro's number: $N = 6.02 \times 10^{23}$

Ideal gas constant: $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

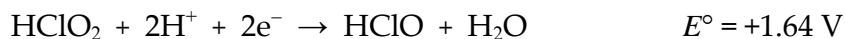
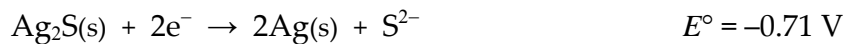
Vapour pressure of water at 27°C : 26.7 mm Hg

4. Draw a diagram of the cell and give a cell notation diagram for the standard galvanic cell you would construct based on each of the following balanced redox reactions.

(Label all parts of your cell diagram and indicate the direction of electron flow.)



5. Use the following standard reduction potentials and Table 18.1 in your textbook to calculate the standard cell potential, E° , for each of the cells in Question 4 above. Are all the given equations spontaneous in the direction written? Briefly explain your answer.



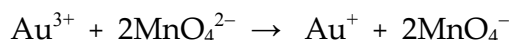
6. Given the standard reduction potentials



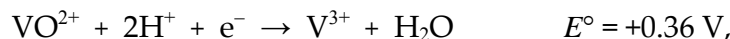
and



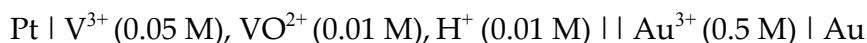
calculate ΔG° and K at 298 K for the reaction



7. Given the standard reduction potential



calculate the cell potential, E , for the electrochemical cell shown in the following cell notation

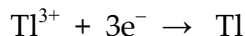


8. a. Determine the cell potential of a cell prepared from two $\text{Ga}^{3+} / \text{Ga}$ half-cells. In one $[\text{Ga}^{3+}] = 2.00 \text{ M}$, and in the other $[\text{Ga}^{3+}] = 0.300 \text{ M}$.

b. Write an equation for this “cell reaction.” Does the oxidation reaction occur at the

0.300 M electrode or the 2.00 M electrode? Briefly explain your answer.

9. A non-standard thallium half-cell, $\text{Tl} / \text{Tl}^{3+} (0.01 \text{ M})$, was connected with a hydrogen half-cell where the pressure of the hydrogen gas was 2.50 atm and the half-cell pH was 1.0. A potential difference of 0.72 V was measured between the two half-cells. At the end of the experiment the pH of the hydrogen half-cell had dropped. From this information, calculate a value for the standard reduction potential of the thallium half-reaction



Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Most selected exercises at the ends of the chapters have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 4:

4.39, 4.40, 4.41, 4.42, 4.43, 4.45, 4.48, 4.52

From Chapter 18:

18.1, 18.2, 18.11, 18.12, 18.13, 18.16, 18.18, 18.24, 18.26, 18.27, 18.31, 18.32, 18.34, 18.35, 18.47, 18.48, 18.50, 18.51, 18.52, 18.56, 18.60, 18.67, 18.68, 18.71, 18.75, 18.79, 18.84, 18.92

Assignment 6

Now refer to your *Assignments* and complete Assignment 6. Consult your Course Manual for the week this assignment is due. Send the assignment to your Open Learning Faculty Member. You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form. Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.