SCH4U

Grade 12
University Chemistry

Lesson 13 – Oxidation and Reduction Rates

Unit 4: Electrochemistry

The interconnection between electricity and chemical reactions is called **electrochemistry**. Specifically electrochemistry deals with the transfer of electrons from one substance to another. These reactions can produce electricity in a spontaneous and a non-spontaneous manner. In this unit you will learn about two important chemical reactions involving the transfer of electrons: oxidation and reduction. You will also learn about how the energy is harvested from oxidation and reduction reactions using special cells called galvanic and electrolytic cells. Practical application of electrochemistry will also be taught.

Overall Expectations

- demonstrate an understanding of fundamental concepts related to oxidation-reduction and the inter-conversion of chemical and electrical energy;
- build and explain the functioning of simple galvanic and electrolytic cells; use equations to describe these cells; and solve quantitative problems related to electrolysis;
- describe some uses of batteries and fuel cells; explain the importance of electrochemical technology to the production and protection of metals; and assess environmental and safety issues associated with these technologies.

Lesson 13: Oxidation and Reduction Reactions

This lesson introduces the fundamental concept of electrochemistry: transfer of electrons. Electron transfer occurs by two important reactions called oxidation and reduction reactions. These reactions often occur in conjunction with one another and hence are termed REDOX reactions. In this lesson you will learn how to identify oxidation and reduction reactions.

What You Will Learn

After completing this lesson, you will be able to

- use appropriate scientific vocabulary to communicate ideas related to electrochemistry (e.g., half-reaction, electrochemical cell, reducing agent, redox reaction, oxidation number);
- demonstrate an understanding of oxidation and reduction in terms of the loss and the gain of electrons or change in oxidation number;
- write balanced chemical equations for oxidation-reduction systems, including half-cell reactions;

Oxidation and Reduction Reactions

As previously mentioned, oxidation and reduction reactions involve the transfer of electrons. In order to explain this, let's look at a sample chemical reaction.

Consider:

Overall Equation

$Zn_{(s)} + CuSO_{4(aq)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$

Total Ionic Equation

$Zn_{(s)} + Cu^{2+}_{(aq)} + \cancel{SO_4^{2-}}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)} + \cancel{SO_4^{2-}{}_{(aq)}}$

Net Ionic Equation

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

Notice what happens to the reactants in this equation.

The zinc atoms **lose** electrons to form zinc ions. ($Zn_{(s)} \rightarrow Zn^{+2}_{(aq)}$)
The copper ions **gain** electrons to form copper atoms. ($Cu^{2+}_{(aq)} \rightarrow Cu_{(s)}$)

An **oxidation** reaction describes a loss of electrons, while a **reduction** reaction occurs when there is a gain of electrons. These reactions always occur in tandem and hence are referred to as **REDOX** reactions.

Identifying Oxidation and Reduction Reactions

Example 1:

Identify the reactant oxidized and the reactant reduced in the following reaction:

$\mathbf{Pb_{(s)} + Cu(NO_3)_{2(aq)} \rightarrow Cu_{(s)} + Pb(NO_3)_{2(aq)}}$

Solution 1:

Step 1: Write the total ionic equation.

$Pb_{(s)} + Cu^{2+} + 2NO_3^-{}_{(aq)} \rightarrow Cu_{(s)} + Pb^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)}$

Step 2: Write the net ionic equation

$Pb_{(s)} + Cu^{2+} + \cancel{2NO_3^-{}_{(aq)}} \rightarrow Cu_{(s)} + Pb^{2+}{}_{(aq)} + \cancel{2NO_3^-{}_{(aq)}}$
$Pb_{(s)} + Cu^{2+} \rightarrow Cu_{(s)} + Pb^{2+}{}_{(aq)}$

Step 3: Identify the charge on each element

$Pb_{(s)} \rightarrow Pb^{2+}$ (oxidized)
$Cu^{2+} \rightarrow Cu(s)$ (reduced)

One easy way of remembering REDOX reactions is the expression

“Leo the Lion says Ger”

Meaning:
Lose **E**lectrons **O**xidation, **G**ain **E**lectrons, **R**eduction

Losing electrons causes an increase in the oxidation number (i.e. 0 → +2)
Gaining electrons causes a decrease in the oxidation number (i.e. +2 →0)

The total number of electrons gained in a reaction must equal the total number of electrons lost.

Support Questions

1. Identify the reactant oxidized and the reactant reduced in each of the following reactions:

   a) $CuCl_{2(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnCl_{2(aq)}$
   b) $2Ag_{(s)} + S_{(s)} \rightarrow Ag_2S_{(s)}$
   c) $CuSO_{4(aq)} + Mg_{(s)} \rightarrow Cu_{(s)} + MgSO_{4(aq)}$

Redox Reactions of Nonmetals

The REDOX reactions that you have learned so far involve metals. In this section you will learn about REDOX reactions that occur in non-metals. In unit one you learned that an ionic bond involves a transfer of electrons between a metal and a non-metal. However, in a covalent bond, electrons are shared, and not fully transferred. Consider the covalent compound carbon dioxide, CO_2. The electrons are shared in a double covalent bond. Chemists still find it useful to assign an apparent charge on each atom. This apparent charge is called an **oxidation number.**

Oxidation Numbers

When we examine the electronegativity difference between carbon and oxygen in carbon dioxide, we note that oxygen is more electronegative than carbon. Since oxygen gains two electrons to become O_2^{2-} (in ionic compounds), the oxygen is assigned an oxidation number of -2. All oxidation numbers must add up to be 0. Knowing this and that the oxidation number of oxygen is -2, we can then determine the oxidation number of the carbon atom in the compound:

$$C + 2(-2) = 0$$
$$C = +4$$

Therefore carbon has an oxidation number of +4.

Assigning oxidation numbers is not an exact science, but the table following gives some general rules and guidelines.

Table 13.1: Rules for Assigning Oxidation Numbers

Rule	Examples
1. The oxidation number of an atom in an **uncombined state** is always 0.	K, O_2, N, Li, etc all have an oxidation number of 0.
2. The oxidation number of a simple ion is the charge of the ion.	The oxidation number of Mg in Mg^{2+} is +2
3. The oxidation number of hydrogen in most compounds is +1 Exception: metal hydrides	The oxidation number of H in H_2O, HCl, HNO_3 is +1 The oxidation number if H in sodium hydride, NaH is -1
4. The oxidation number of oxygen in most compound is -2	The oxidation number of O in H_2O, MgO and HNO_3 is -2 The oxidation number of O in hydrogen peroxide, H_2O_2 is -1
5. The oxidation number of Group 1 element ions is +1. The oxidation number of Group II element ions is +2	The oxidation number of K in K+ is +1. The oxidation number of Mg in Mg2+ is +2
6. The sum of oxidation number in a compound must equal 0.	In H_2O 2(+1) + (-2) = 0
7. The sum of oxidation numbers in a polyatomic ion must equal the charge of the ion.	In hydroxide, OH^- (-2) + (+1) = -1

Example 2:

Determine the oxidation number of the nitrogen atom in Lithium nitrate, $LiNO_3$.

Solution 2:

Step 1: Write all known oxidation numbers, let x be the oxidation number for nitrogen

Li	N	O_3
+1	**x**	**-2**

Step 2: Multiply oxidation number by number of each type of atom

Li	N	O_3
+1	x	3(-2)

Step 3: Solve for the unknown oxidation number

$$(+1) + x + 3(-2) = 0$$
$$x - 5 = 0$$
$$x = +5$$

Support Questions

2. Assign oxidation numbers to each atom in $NiCl_2$, $Mg_{(s)}$, TiO_4, $K_2Cr_2O_7$, SO_3^{2-}.

3. Assign oxidation numbers to the underlined atoms. (a) $\underline{Cl}O_4^-$, (b) $\underline{Cr}Cl_3$, (c) $\underline{Sn}S_2$, (d) $\underline{Au}(NO_3)_3$.

4. Assign oxidation numbers to the elements in the following: (a) $SnCl_4$, (b) MnO_4^-, (c) MnO_2.

5. Molybdenum disulphide, MoS_2, has a structure that allows it to behave as a dry lubricant, much like graphite. What are the oxidation numbers of the atoms in MoS_2?

REDOX Reaction or Not?

Perhaps the one of the most useful applications of oxidation numbers is to determine if a REDOX reaction has occurred or not. In order for a REDOX reaction to have occurred, there must have been

- An oxidation number decrease (reduction)
- An oxidation number increase (oxidation)

Example 3:

In each of the following reactions, determine if a REDOX reaction has occurred:

a) $Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$
b) $SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$

Solution 3:

a) Step 1: Write all known oxidation numbers

$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$
0 0 +2-2

Zinc changes from 0 to +2
Sulphur changes from 0 to -2
Therefore this is a REDOX reaction

$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$

b) Step 1: Write all known oxidation numbers, let x represent unknown oxidation numbers, and solve for unknown oxidation numbers

S	$O_{3(g)}$ +	H_2	$O_{(l)}$ →	H_2	S	$O_{4(aq)}$
X	**3(-2)**	**2(+1)**	**-2**	**2(+1)**	**X**	**4(-2)**

$$x - 6 = 0 \qquad\qquad 2 + x - 8 = 0$$
$$x = 6 \qquad\qquad x = 6$$

Since there is no change in oxidation number for any of the atoms, this is not a REDOX reaction.

Support Questions

6. Which of the following equations represent REDOX reactions? Which do not represent REDOX reactions? Prove your answer with oxidation numbers

   a) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
   b) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
   c) $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$
   d) $2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2LiOH_{(aq)} + H_{2(g)}$
   e) $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$

Balancing Redox Reactions

Simple redox reactions can be balanced by inspection or trial-and-error method. In more complex chemical reactions, oxidation numbers and half-reaction equations can be used to balance any redox equation.

Oxidation Number Method

The increase in oxidation number for an atom/ion must equal the decrease in the oxidation number of another atom/ion.

In more simple terms, the increase and subsequent decrease oxidation numbers must be the same. Let's try an example to illustrate this:

Example 4:

Balance the following redox equation using the oxidation number method. Be sure to check that the atoms and the charge are balanced.

$$HNO_{3(aq)} + H_3AsO_{3(aq)} \rightarrow NO_{(g)} + H_3AsO_{4(aq)} + H_2O_{(l)}$$

Solution 4:

Step 1: Verify that this reaction is a REDOX reaction

→ The nitrogen atoms change from +5(reactant side) to +2(product side), so they are reduced.
→ The arsenic atoms, change from +3(reactant side) to +5 (product side), are oxidized.

Therefore this is a REDOX reaction

Step 2: Determine the net increase in oxidation number for the element that is oxidized and the net decrease in oxidation number for the element that is reduced.

As +3 to +5 Net Change = +2

N +5 to +2 Net Change = -3

Step 3: Determine a ratio of oxidized to reduced atoms that would yield a net increase in oxidation number **equal** to the net decrease in oxidation number.

Three arsenic atoms would yield a net increase in oxidation number of +6. (Six electrons would be lost by three arsenic atoms.) Two nitrogen atoms would yield a net decrease of -6. (Two nitrogen atoms would gain six electrons.) Thus the ratio of arsenic atoms to nitrogen atoms is 3:2.

Step 4: To obtain the ratio identified in Step 3, add coefficients to the formulas which contain the elements whose oxidation number is changing.

$\mathbf{2}HNO_{3(aq)} + \mathbf{3}H_3AsO_{3(aq)} \rightarrow NO_{(g)} + H_3AsO_{4(aq)} + H_2O_{(l)}$

Step 5:
Balance the rest of the equation by inspection.

$2HNO_{3(aq)} + 3H_3AsO_{3(aq)} \rightarrow 2NO_{(g)} + 3H_3AsO_{4(aq)} + H_2O_{(l)}$

In some REDOX reactions that occur in acidic or basic Solutions, you may need to add water molecules, hydrogen ions, or hydroxide ions to balance the equation.

Example 5:
Chlorate ions and iodine react in an acidic solution to produce chloride ions and iodate ions.

Solution 5:

$ClO_3^-{}_{(aq)} + I_{2(aq)} \rightarrow Cl^-{}_{(aq)} + IO_{3(aq)}^-$

We will combine some steps used in the previous example to condense our solution

Steps 1 and 2: Determine if the reaction is a REDOX reaction and the net change

Reduction → Chlorine +5(reactant side) to -1(product side)
The net change is -6

Oxidation → Iodine 0 (reactant side) to +5 (product side)
The net change is +5

Step 3: Determine a ratio of oxidized to reduced atoms that would yield a net increase in oxidation number **equal** to the net decrease in oxidation number.

Five chlorine atoms would yield a net decrease in oxidation number of -30. Six iodine atoms would yield a net increase of +30.

Step 4: To obtain the ratio identified in Step 3, add coefficients to the formulas which contain the elements whose oxidation number is changing. **Note in this case there are 5 electrons per iodine(I) (i.e. 5 x6=30electrons), and 10 electrons per iodine molecule (I_2) (i.e. 10 x 3=30 electrons), so a 3 will be used on the reactant side of the equation.**

$5ClO_3^-{}_{(aq)} + 3I_{2(aq)} \rightarrow 5\ Cl^-{}_{(aq)} + 6IO_{3(aq)}^-$

Step 5: You may notice that although the chlorine or iodine is balanced, the oxygen is not. Since this reaction occurs is aqueous, we can add water to balance the O atoms. In this case, the reactant side is short 3 oxygen atoms, so three water molecules can be added to balance this.

$5ClO_3^-{}_{(aq)} + 3I_{2(aq)} + 3H_2O_{(l)} \rightarrow 5\ Cl^-{}_{(aq)} + 6IO_{3(aq)}^-$

Step 6: Add hydrogen ions to balance the H atoms. In this case, we need to add 6 H+ ions to balance the equation

$5ClO_3^-{}_{(aq)} + 3I_{2(aq)} + 3H_2O_{(l)} \rightarrow 5\ Cl^-{}_{(aq)} + 6IO_{3(aq)}^- + 6H^+{}_{(aq)}$

The method is slightly different for a basic solution. Let’s try an example

Example 6:

Methanol reacts with permanganate ions in a basic solution. The main reactants and products are shown below.

Solution 6:

$CH_3OH_{(aq)} + MnO_4^-{}_{(aq)}$- → $CO_3^{2-}{}_{(aq)} + MnO_4^{2-}{}_{(aq)}$

Steps 1: Determine if the reaction is a REDOX reaction and the net change

→ Oxidation – Carbon is -2(reactant side) and +4(product side)
Net change +6

→Reduction- Manganese is +7 (reactant side) to +6 (product side)
Net change -1

Step 2: Determine a ratio of oxidized to reduced atoms that would yield a net increase in oxidation number **equal** to the net decrease in oxidation number.

One carbon atoms would yield a net increase of 6 electrons, and 6 manganese atoms would yield a net decrease of 6 electrons.

Step 3: To obtain the ratio identified in Step 2, add coefficients to the formulas which contain the elements whose oxidation number is changing

$CH_3OH_{(aq)} + \mathbf{6}MnO_4^-{}_{(aq)}$- → $CO_3^{2-}{}_{(aq)} + \mathbf{6}MnO_4^{2-}{}_{(aq)}$

Step 4: Add water and to balance the oxygen atoms, and then H^+ to balance the hydrogen atoms.

$\mathbf{2H_2O_{(l)}} + CH_3OH_{(aq)} + 6MnO_4^-{}_{(aq)}{}^- \rightarrow CO_3^{2-}{}_{(aq)} + 6MnO_4^{2-}{}_{(aq)} + \mathbf{8H^+{}_{(aq)}}$

Step 5: In basic solutions, we add enough OH to the reaction to equal the number of H^+ present, which in this case is 8.

$\mathbf{8OH^-}{}_{(aq)} + 2H_2O_{(l)} + CH_3OH_{(aq)} + 6MnO_4^-{}_{(aq)}{}^- \rightarrow CO_3^{2-}{}_{(aq)} + 6MnO_4^{2-}{}_{(aq)} + 8H^+{}_{(aq)} + \mathbf{8OH^-}{}_{(aq)}$

Step 6: Cancel out the water on both sides. Note that the $8H^+$ and $8OH^-$ form 8 water molecules. Write your final reaction.

$8OH^-{}_{(aq)} + CH_3OH_{(aq)} + 6MnO_4^-{}_{(aq)}{}^- \rightarrow CO_3^{2-}{}_{(aq)} + 6MnO_4^{2-}{}_{(aq)} + 6H_2O_{(l)}$

Support Questions

7. Balance the following redox equations using the oxidation number method.

   a) $Al_{(s)} + MnO_{2(s)} \rightarrow Al_2O_{3(s)} + Mn_{(s)}$
   b) $SO_{2(g)} + HNO_{2(aq)} \rightarrow H_2SO_{4(aq)} + NO_{(g)}$
   c) $HNO_{3(aq)} + H_2S_{(aq)} \rightarrow NO_{(g)} + S_{(s)} + H_2O_{(l)}$
   d) $Al_{(s)} + H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + H_{2(g)}$

8. Balance the following redox reactions using the oxidation number method

   a) $Cr_2O_7^{2-}{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow Cr^{3+}{}_{(aq)} + Cl_{2(aq)}$ (in acidic solution)
   b) $MnO_4^-{}_{(aq)} + SO_3^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + MnO_{2(s)}$ (in basic solution)

The Half-Reaction Method for Balancing Equations

Another method for balancing REDOX reactions is the half-reaction method. In this method, the half-reactions are obtained, and the electrons are balanced.

Balancing Half-Reactions in Acidic Solutions

- Write unbalanced half-reactions
- Balance any atoms other than oxygen and hydrogen
- Balance any oxygen atoms by adding water molecules
- Balance any hydrogen atoms by adding hydrogen ions
- Balance electron charges
- Add half cell reactions

Example 7:

Balance the following equation in acidic solution:

$Fe^{2+}{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + Cr^{3+}{}_{(aq)}$

Solution 7:

First write out the unbalanced half reaction.

$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)}$
$Cr_2O_7^{2-}{}_{(aq)} \rightarrow Cr^{3+}{}_{(aq)}$

Treat each half reaction separately to obtain a balanced equation.

For the iron(II) half reaction you just need to add an electron to balance the charge.

$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e-$

For the dichromate half-reaction, balance the oxygen by adding water molecules, then balance the hydrogen atoms with hydrogen ions, and finally balance the electron charges.

$6e^{-} + 14H^{+}{}_{(aq)} + Cr_2O_7{}^{2-}{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

In order to balance the equation, multiply one or both of the half reactions to balance the electron charges. In this case, the iron (II) half reaction must be multiplied by six.

$6Fe^{2+}{}_{(aq)} \rightarrow 6Fe^{3+}{}_{(aq)} + 6e-$

Now add the two half-cell reactions.

$6Fe^{2+}{}_{(aq)} + \cancel{6e^{-}} + 14H^{+}{}_{(aq)} + Cr_2O_7{}^{2-}{}_{(aq)} \rightarrow 6Fe^{3+}{}_{(aq)} + \cancel{6e-} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

$6Fe^{2+}{}_{(aq)} + 14H^{+}{}_{(aq)} + Cr_2O_7{}^{2-}{}_{(aq)} \rightarrow 6Fe^{3+}{}_{(aq)} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

Balancing Half-Reactions in Basic Solutions

- Follow procedure for half-reactions in Acidic Solutions
- Adjust for Basic Solution by adding to both sides the same number of hydroxide ions as the number of hydrogen ions already present
- Simplify the half-reaction by combining H^{+} and OH^{-} to form H_2O
- Cancel out any H_2O molecules present on both sides of the half-reaction
- Balance the charges by adding electrons

NOTE: once the oxidation half-reaction and reduction half-reaction are balanced independently, they can be combined using the lowest common multiple of the number of electrons

Support Questions

9. Balance the following redox equations (using the half cell method) for reactions run in acidic conditions.

   a) $MnO_4{}^{-}{}_{(aq)} + Br^{-}{}_{(aq)} \rightarrow MnO_{2(s)} + BrO_3{}^{-}{}_{(aq)}$
   b) $I_{2(s)} + OCl^{-}{}_{(aq)} \rightarrow IO_3{}^{-}{}_{(aq)} + Cl^{-}{}_{(aq)}$
   c) $Cr_2O_7{}^{2-}{}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \rightarrow Cr^{3+}{}_{(aq)} + CO_{2(g)}$
   d) $Mn_{(s)} + HNO_{3(aq)} \rightarrow Mn^{2+}{}_{(aq)} + NO_{2(g)}$

10. Balance the following redox equations (using the half cell method) for reactions run in basic conditions.

a) $CrO_4{}^{2-}{}_{(aq)}$ + $S^{2-}{}_{(aq)}$ → $Cr(OH)_{3(s)}$ + $S_{(s)}$
b) $MnO_4{}^{-}{}_{(aq)}$ + $I^{-}{}_{(aq)}$ → $MnO_{2(s)}$ + $IO_3{}^{-}{}_{(aq)}$
c) $H_2O_{2(aq)}$ + $ClO_4{}^{-}{}_{(aq)}$ → $O_{2(g)}$ + $ClO_2{}^{-}{}_{(aq)}$
d) $S^{2-}{}_{(aq)}$ + $I_{2(s)}$ → $SO_4{}^{2-}{}_{(aq)}$ + $I^{-}{}_{(aq)}$

Key Question #13

1. Consider the following ion

$XF_2{}^{-2}$

What is the oxidation number assigned to element “X”? Show your work. (2 marks)

2. Determine the oxidation number of the underlined element in each of the following. (9 marks)

a) $\underline{O}_2$
b) $\underline{Ag}NO_3$
c) $\underline{Mn}O_2$
d) $\underline{Zn}SO_4$
e) $\underline{Cl}O_3$-
f) $\underline{C}O_3{}^{2-}$
g) $K\underline{Mn}O_4$
h) $Mg\underline{S}O_3$
i) $Na_2\underline{S}_2O_3$

3. Consider the following reaction for silver tarnishing:

$3Ag_2S_{(s)} + 2Al_{(s)} \rightarrow 6Ag_{(s)} + Al_2S_{3(s)}$

a) State the oxidation number for each element in the reaction. (3 marks)
b) Identify the oxidized reactant and the reduced reactant. (2 marks)

4. The following reactions are involved in the formation of acid rain. Use oxidation numbers to identify which of these reactions are REDOX reactions. (6 marks)

a) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{2(g)}$
b) $3NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$
c) $SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$

5. Use the oxidation method to balance the following reactions. (6 marks)

a) $IO_3{}^{-}{}_{(aq)} + HSO_3{}^{-}{}_{(aq)} \rightarrow SO_4{}^{2-}{}_{(aq)} + I_{2(s)}$ (in acidic solution)
b) $ClO_3{}^{-}{}_{(aq)} + N_2H_{4(aq)} \rightarrow NO_{(g)} + Cl^{-}{}_{(aq)}$ (in basic solution)

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Grade 12
University Chemistry

Lesson 14 – The Activity Series of Metals

Lesson 14: The Activity Series of Metals

Metals tend to react by losing electrons. Some metals however will lose electrons more readily than other metals. How reactive a metal is will help chemists predict whether a reaction will occur spontaneously or not. In this lesson you will learn about a ranking chart for metals that chemists use called the **activity series of metals**. You will then predict the spontaneity of various chemical reactions using the activity series.

What You Will Learn

After completing this lesson, you will be able to

- use appropriate scientific vocabulary to communicate ideas related to electrochemistry (e.g., half-reaction, electrochemical cell, reducing agent, redox reaction, oxidation number);
- predict the spontaneity of redox reactions

Conductors vs. Non-Conductors

A **conductor** is capable of conducting electricity whereas a **non-conductor** is not. As you may know, the human body is mostly water, and it is a relatively good conductor of electricity. For this reason we must use caution whenever using electrical devices around water. You may be surprised then to learn that pure distilled water does not conduct electricity. It is the ions present in water that allow the flow of electrons or electricity in water. Human blood is mostly water and dissolved ions that allow a good flow of electricity.

Generally substances that can ionize are conductors. Let's look at some examples.

Acidic ions: $H_2SO_{4(g)} \rightarrow 2H^+_{(aq)} + SO^{2-}_{4(aq)}$
Basic ions: $Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$
Salt ions: $NaCl_{(s)} \rightarrow Na^{+1(}{}_{aq)} + Cl^-_{(aq)}$

In addition to chemicals that can ionize, metals are able to conduct electricity. Metals conduct electricity by passing the charge through a pool of electrons.

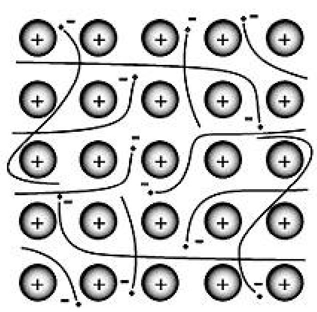

Figure 18.1: Electrons can move freely in a sea of positive ions in metals.

Ionic compounds also ionize to conduct electricity and are often termed electrolytes. It is important to note that ionic compounds only conduct electricity when they are in their aqueous ionized form.

$NaNO_{3(s)} \rightarrow Na^{+1}_{(aq)} + NO_{3}^{-}{}_{(aq)}$

In the reaction above, solid sodium nitrate ($NaNO_{3(s)}$) does not conduct electricity, whereas the aqueous ions, sodium (Na^{+1}) and nitrate (NO_3^{-1}) are excellent conductors. Non-conductors or non-electrolytes include substances that do not ionize. Examples include alcohol, sugar and water, and other covalent molecules.

Example 1:

Determine of the following substances can conduct electricity in the form shown.

a) $CuCl_{2(aq)}$
b) $NaOH_{(s)}$
c) $H_2O_{(l)}$
d) $CH_3OH_{(aq)}$
e) $HCl_{(aq)}$

Solution 1:

a) Conductor – This is an aqueous ionic compound
b) Non-conductor – Solid ionic compound (it is not ionized)
c) Non-conductor – Pure distilled water has no ions
d) Non-conductor – Covalent compounds are non-conductors
e) Conductors – Aqueous acids are conductors

Support Questions

11. Determine which of the following substances can conduct electricity in the form shown.

a) $ZnSO_{4(aq)}$
b) $LiOH_{(s)}$
c) $H_2O_{(l)}$
d) $C_6H_{12}O_{6(aq)}$
e) $HBr_{(aq)}$

The Activity Series for Metals

Have you ever wondered why expensive jewellery is made of expensive metals such as gold that never seem to tarnish? Often costume jewellery will tarnish and change colour over time. Electrochemistry can be used to explain why some metals readily react whereas others do not.

An **activity series** is a list of substances ranked in order of relative reactivity. For example, magnesium metal can displace hydrogen ions out of solution, so it is considered more reactive than hydrogen:

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

Zinc can also displace hydrogen ions from solution:

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

This means that zinc is also more active than hydrogen. But magnesium metal can remove zinc ions from solution:

$$Mg_{(s)} + Zn^{2+}_{(aq)} \rightarrow Zn_{(s)} + Mg^{2+}_{(aq)}$$

Magnesium is more active than zinc, and the activity series including these elements would be Mg > Zn > H. The activity series (table 18.1) was constructed in a similar manner by experimentation by chemists. The most active metals are at the top of the table; the least active are at the bottom. Each metal is able to displace the elements below it from solution (or, using the language of electrochemistry, each metal can reduce the cations of metals below it to their elemental forms).

Most reactive (easily oxidized)

Lithium
Potassium
Barium
Calcium
Sodium
Magnesium
Aluminum
Zinc
Chromium
Iron
Cadmium
Colbalt
Nickel
Tin
Lead
Hydrogen*
Copper/Silver
Platinum
Gold

Least oxidized (not easily oxidized)

*Hydrogen is the only non-metal included in the metallic activity series,

You can use the activity series to predict the products of a single displacement reaction.

$$\mathbf{A} + BC \rightarrow \mathbf{A}C + B$$

In the example above, the element “A” displaces the element “B” to reform compound “AC”. The activity series can be used to determine if a single displacement reaction will occur or not. In general, an element that is higher in the activity series will displace an element that is lower. When an element displaces an element lower than it on the activity series, it is called a **spontaneous reaction**.

Example 2:

Predict whether a chemical reaction will occur in each of the following reactions.

Solution 2:

a) $Al_{(s)} + AgNO_{3(aq)} \rightarrow$

In the reaction above, aluminum is above silver in the activity series, and thus a reaction will occur.

$Al_{(s)} + 3AgNO_{3(aq)} \rightarrow 3Ag_{(s)} + Al(NO_3)_{3(aq)}$

b) $Cu_{(s)} + FeSO_{4(aq)} \rightarrow$

In this example, copper is below iron in the activity series, and therefore no reaction will occur.

$Cu_{(s)} + FeSO_{4(aq)} \rightarrow$ no reaction

Support Questions

12. Use the activity series to predict if a reaction will occur or not. If a reaction occurs, complete and balance your equation.

    a) $Zn_{(s)} + AgCl_{(aq)} \rightarrow$
    b) $Cu_{(s)} + Sn(NO_3)_{2\ (aq)} \rightarrow$
    c) $Mg_{(s)} + H_2SO_{4(aq)} \rightarrow$
    d) $Ag_{(s)} + HNO_{3(aq)} \rightarrow$
    e) $Zn_{(s)} + FeCO_{3(aq)} \rightarrow$

Key Question #14

1. Use the activity series to predict if a reaction will occur or not. If a reaction occurs, complete and balance your equation. (10 marks)

    a) $Zn_{(s)} + Cu(NO_3)_{2(aq)} \rightarrow$
    b) $Au_{(s)} + FeSO_{4(aq)} \rightarrow$
    c) $Zn_{(s)} + HCl_{(aq)} \rightarrow$
    d) $Pb_{(s)} + Ni(NO_{3)2(aq)} \rightarrow$
    e) $Mg_{(s)} + H_2SO_{4(aq)} \rightarrow$

2. Consider the following lab data, gathered from two different lab students:

Student 1: Lab data for the determination of an activity series of metals

Chemical	$Ag^{+}_{(aq)}$	$Ni^{2+}_{(aq)}$	$Pb^{+2}_{(aq)}$	$Zn^{+2}_{(aq)}$
$Ag_{(s)}$		No change	No change	No change
$Ni_{(s)}$	Grey coating forms on nickel		Black coating forms on nickel	No change
$Pb_{(s)}$	Grey coating forms on lead	No change		No change
$Zn_{(s)}$	Grey coating forms on zinc	Grey coating forms on zinc	Black coating forms on zinc	

Student 2: Lab data for the determination of an activity series of metals

Chemical	$Ag^{+}_{(aq)}$	$Ni^{2+}_{(aq)}$	$Pb^{+2}_{(aq)}$	$Zn^{+2}_{(aq)}$
$Ag_{(s)}$		Grey coating forms on silver	Black coating forms on silver	Grey coating forms on silver
$Ni_{(s)}$	Grey coating forms on nickel		No change	No change
$Pb_{(s)}$	Grey coating forms on lead	Grey coating forms on lead		No change
$Zn_{(s)}$	No change	No change	No change	

a) Which student has valid results? (2 marks)
b) Justify your answer by stating the errors in the incorrect observation table. (4 marks)
c) Suggest two reasons why a student may experience poor results during this type of chemical experiment. Any two reasonable explanations related to the experiment, such as the following reasons. (2 Marks)

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Grade 12
University Chemistry

Lesson 15 – Galvanic Cells

Lesson 15: Galvanic Cells

You have learned that electrochemistry deals with the spontaneous transfer of electrons from one substance to another. Many REDOX reactions will occur spontaneously, and energy can be harvested from these reactions. In this lesson you will learn how energy can be harvested through special cells called **galvanic cells**, and practical applications of galvanic cells.

What You Will Learn

After completing this lesson, you will be able to

- identify and describe the functioning of the components in galvanic cells
- describe electrochemical cells in terms of oxidation and reduction half-cells whose voltages can be used to determine overall cell potential;
- describe examples of common galvanic cells (e.g., lead-acid, nickel-cadmium) and evaluate their environmental and social impact (e.g., describe how advances in the hydrogen fuel cell have facilitated the introduction of electric cars);
- explain corrosion as an electrochemical process, and describe corrosion-inhibiting techniques (e.g., painting, galvanizing, cathodic protection).
- predict the spontaneity of redox reactions and overall cell potentials by studying a table of half-cell reduction potentials;

Electrochemistry and Batteries

Recall the reaction between zinc metal and copper II ions you learned in lesson 13;

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

In this REDOX reaction, the zinc atoms **lose** electrons to become oxidized and copper II ions **gain** electrons to become reduced.
This reaction can be further simplified into a **half-reaction**.

Half Reactions

A half reaction shows either the reactant that is oxidized or the reactant that is reduced. Two half-reactions are needed to represent a complete REDOX reaction (one shows oxidation, the other shows reduction) In a half reaction, the atoms **and** charges must balance and the coefficients must be in smallest whole-number ratio.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \text{ (oxidation)}$$

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)} \text{ (reduction)}$$

Wet Galvanic Cells (Voltaic Cells)

A galvanic cell is a device that **spontaneously** converts chemical energy to electrical energy. In a galvanic cell, electrons flow from one reactant to the other through an external circuit. A porous barrier (or a salt bridge) separates the two half-cells. The oxidation half-reaction occurs in one half-cell and the reduction half-reaction occurs in the other half-cell. Each half cell contains an aqueous solution. Figure 15.1 below depicts a basic galvanic cell.

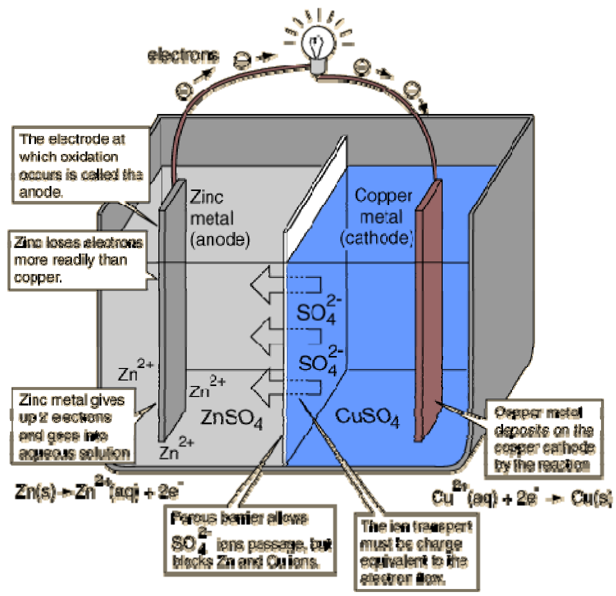
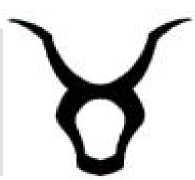


Figure 15.1: A Galvanic Cell

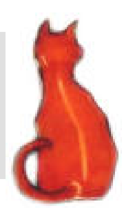
The reactants must be separated in order to retain the full electric potential of a spontaneous reaction. For this reason, a galvanic cell contains two beakers, each with its own electrolyte solution. The immersed conductors carry electrons into and out of the connecting wires called **electrodes**.   The electrodes have two names: the **anode** and the **cathode**. At the anode, electrons are released by oxidation reaction. At the cathode electrons are used in reduction reaction.

Here is a memory tip for remembering the anode and cathode;



Anode (An Ox)

Cathode (Red Cat)



Since drawing galvanic cells can be time consuming, shorthand notation is often used to represent the cell:

Zn | Zn^{2+} || Cu^{2+} | Cu
Anode Bridge | Cathode

General guidelines when using the shorthand method include:

- Anode is always shown on the left (Zn)
- Cathode is always shown on the right (Cu)
- The double bar represents the barrier or salt bridge
- Solutions are on each side of the double bar

Example 1:

Consider the following REDOX reaction:

$Ni_{(s)} + Cu^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Cu_{(s)}$

a) Write the oxidation and reduction half reaction.
b) Show this reaction in shorthand notation.

Solution 1:

First assign oxidation number to determine oxidation and reduction:

$Ni_{(s)} + Cu^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Cu_{(s)}$
0 +2 +2 0

In the above reaction nickel is oxidized and copper is reduced.

$Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Shorthand notation

$Ni_{(s)}\ |Ni^{2+}_{(aq)}\ ||\ Cu^{2+}_{(aq)}\ |\ Cu_{(s)}$

Support Questions

13. Consider the following REDOX reaction:

$$Zn_{(s)} + Fe^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Fe_{(s)}$$

a) Write the oxidation and reduction half reaction.
b) Show this reaction in shorthand notation.

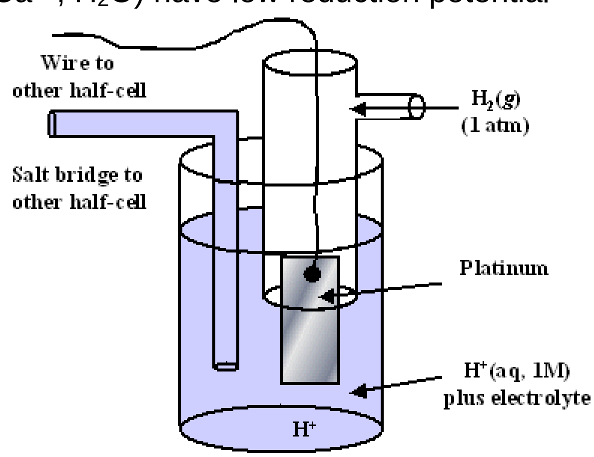
Standard Cells and Cell Potentials

A standard cell is a galvanic cell in which each half-cell contains all components shown in a half cell reaction at SATP (Standard temperature and pressure), with a concentration of 1.0mol/L for the aqueous solutions.

Cell Potential

The difference between the potential energies at the anode and the cathode is called the **cell potential.** Each half-reaction is written as a reduction and thus is called the **reduction potential.** The **standard reduction potential** (E_r^o), represents the ability of a standard half-cell to attract electrons. The half-cell with the greater attraction for electrons gains electrons from the half-cell with the lower reduction potential.

- easily reduced ions/molecules (ie: F_2, MnO_4^-) have high reduction potential
- poorly reduced ions/molecules (ie: Na^+, Ca^{2+}, H_2O) have low reduction potential
- values are for **standard conditions:** standard state, conc. of 1 mol/L, temperature (25^{o}C or 298K) and pressure (101.3kPa or 1 atm)
- values are relative to the standard hydrogen electrode, assigned a value of zero



Example 2:

Anode (OX) Cathode (RED)

$$\mathbf{Zn \mid Zn^{2+}\ (1\ mol/L) \parallel Cu^{2+}\ (1\ mol/L) \mid Cu}$$

Calculate the standard cell potential

Solution 2:

There are two possible solutions to this problem, and are shown in the table below:

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^o = 0.342$ V $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $E^o = -0.762$ V	**GER:** $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^o = 0.342$ V **LEO:** $Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$ $E^o = +0.762$ V
Method 1: $E^o_{cell} = E^o_{Cathode} - E^o_{Anode}$	Method 2: $E^o_{cell} = E^o_{Reduction} + E^o_{Oxidation}$
$= 0.342 \text{ V} - (-0.762 \text{ V})$ $= 0.342 \text{ V} + 0.762 \text{ V}$ $= 1.104$ V	$= 0.342 \text{ V} + 0.762 \text{ V}$ $= 1.104$ V

The standard reduction potential are given values that you can find in Appendix at the end of the Unit Booklet. You will always be provided these values on your exams.

Calculating a Standard Cell Potential

Example 2:

Write the two half-reactions for the following REDOX reaction. Add the standard reduction potential and the standard oxidation potential to find the standard cell potential for the reaction.

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

Solution 2:

Step 1: Write the equation in ionic form to identify the half-reactions.

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

First write the oxidation and reduction half-reactions

Oxidation half reaction (occurs at the anode): $Na_{(s)} \rightarrow Na^+_{(aq)} + e^-$

Reduction half-reaction (occurs at the cathode): $2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$

Step 2: Look up the reduction potentials in a table of standard reduction potentials.

E^o cell = E°cathode – E°anode
E^o cell = -0.828V - (-2.711V)
E^o cell = 1.883V

Support Questions

14. Calculate the standard cell potential for the galvanic cell in which the following reaction occurs.

$$2I^-(aq) + Br_{2(l)} \rightarrow I_{2(s)} + 2Br^-_{(aq)}$$

15. For the following cell, write the equation for the reactions occurring at the cathode and the anode and calculate the standard cell potential.

$Sn \mid Sn^{2+}$ (1mol/L) || Cr^{2+} (1 mol/L) | Cr

Dry Cells and Batteries

Although wet galvanic cells harvest electrical energy, it would be very inconvenient to carry them around for electricity. A more convenient form of portable power is the dry cell or **battery**. A battery is two or more galvanic cells connected in series. There are many different types of batteries cylindrical or rectangular, large and small. Although they vary widely in composition and form, they all work on the sample principle. A "dry-cell" battery is essentially comprised of a metal electrode or graphite rod (carbon) surrounded by a moist electrolyte paste enclosed in a metal cylinder as shown below.

Figure 19.2: A dry cell (battery)

All cells have three basic parts: two electrodes (an anode and a cathode), and an electrolyte. In the diagram above the anode is zinc and the cathode is a mixture of manganese dioxide and carbon. A thin porous fabric keeps the anode and cathode chemicals separate while allowing electrons to pass through it.

The half cell reactions are

Cathode: $2MnO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2MnO_2H_{(s)} + 2OH^-$ (aq)
Anode: $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

A **primary** cell is a cell that cannot be recharged while a **secondary** cell is a rechargeable cell.

Support Questions

16. What are the three component of a dry cell?

17. Explain the difference between wet and dry cells.

Corrosion

Corrosion is a spontaneous REDOX reaction of materials with substances in their environment. Corrosion most often involves metals in contact with oxygen from the atmosphere. For example, if a bicycle is left outside for a long period of time, the chain may rust if the metal reacts with oxygen in the air. Not all corrosion is harmful. For example beautiful green patina (copper II oxide) on a copper roof is the product of corrosion:

$$2Cu^{2+} + O_2 \rightarrow 2CuO$$

Water is needed for rusting to occur. The carbon dioxide in air dissolves in water to form carbonic acid ($H_2CO_{3(aq)}$). Carbonic acid is a weak acid that can turn water into an electrolyte.

The REDOX Chemistry of Rust

A corroding metal is actually a galvanic cell in which one part of the metal is the anode and another part of the metal is the cathode. Let's look at the corrosion of the metal iron for example:

Anode: $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$
Cathode: $\frac{1}{2} O_{2(g)} + H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)}$

There are factors that affect the rate of corrosion such as the amount of moisture (the more moisture, the more corrosion), dissolved electrolytes, contact with less reactive metals, and mechanical stress.

Key Question #15

1. Consider the following REDOX reaction:

   $Zn_{(s)} + Pb^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Pb_{(s)}$

   a) Write the oxidation and reduction half-cell reactions. (4 marks)
   b) Sketch the cell, label the anode and cathode and the direction in which the electrons are flowing. (4 marks)
   c) Show this reaction in shorthand notation. (2 marks)

2. Some people claim that it is better to leave a car outside overnight during the winter, rather than in a warm garage, especially if salt is used on the roads. Give reasons for and against this claim. (4 marks)

3. A voltaic cell is constructed using electrodes based on the following half reactions:

   $Pb^{2+}{}_{(aq)} + 2e- \rightarrow Pb_{(s)}$
   $Au^{3+}{}_{(aq)} +3e- \rightarrow Au_{(s)}$

   a) Which is the anode and which is the cathode in this cell? (2 marks)
   b) What is the standard cell potential? (2 marks)

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Grade 12
University Chemistry

Lesson 16 – Electrolytic Cells

Lesson 16: Electrolytic Cells

In this lesson you will learn about a reaction that is the reverse of the spontaneous reaction that occurs in galvanic cells. This type of reaction occurs in a special cell called an electrolytic cell, and requires the input of electricity. You will learn how electrolytic cells work and practical applications of these cells.

What You Will Learn

After completing this lesson, you will be able to

- identify and describe the functioning of the components in electrolytic cells;
- demonstrate an understanding of the interrelationship of time, current, and the amount of substance produced or consumed in an electrolytic process (Faraday's law);
- solve problems based on Faraday's law;

Electrolytic Cells

- **Galvanic cell** contains a **spontaneous** reaction with electrons flowing from a higher potential to a lower potential, thereby generating electrical energy.
- **Electrolytic cell** uses energy to move electrons from a lower potential energy to a higher potential energy. The overall reaction in an electrolytic cell is **non-spontaneous**, and requires an external source of energy to occur.
- Because of the external voltage of the electrolytic cell, the electrodes do not have the same polarities (charge) in electrolytic and galvanic cells.

"Forcing" a REDOX reaction

The reactions that occur in an electrolytic cell are the reverse of what happens in a galvanic cell. An electrolytic cell requires a power source in order for electrolysis to occur. The power source provides the energy to push electrons towards the cathode and away from the anode. This means that the anode becomes positively charged and the cathode becomes negatively charged. Positive ions move toward the cathode, where reduction occurs. Negative ions move toward the anode where oxidation occurs. For example, consider the reaction between zinc and copper II ions:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

When the reaction moves in the forward direction (from left to right), the reaction is spontaneous and it generates electricity. Zinc is able to displace copper II ions from the solution spontaneously. However, if we consider the reverse, that is, copper II ions displacing zinc, the reaction will not occur spontaneously.

$$Cu_{(s)} + Zn^{2+}_{(aq)} \rightarrow \text{no reaction}$$

Copper, like zinc is a metal. Metals tend to react by losing electrons. Zinc however, loses it electrons more readily. The electrons from zinc overpower the electrons trying to leave the copper electrode. The battery provides the energy to push the electrons away from the copper electrode. The battery is positioned so that the negative end of the battery faces the zinc and the positive end of the battery faces the copper. The flow of electrons in a battery is always from the positive terminal to the negative terminal. This is how the reaction occurs in a non-spontaneous manner.

Comparing Galvanic and Electrolytic Cells

Figure 16.1 is a diagram comparing the galvanic cell to the electrolytic cell. Notice the flow of electrons is reversed in the electrolytic cell. This is due to the presence of the battery. Any galvanic cell can be converted into an electrolytic cell with the presence of a battery.

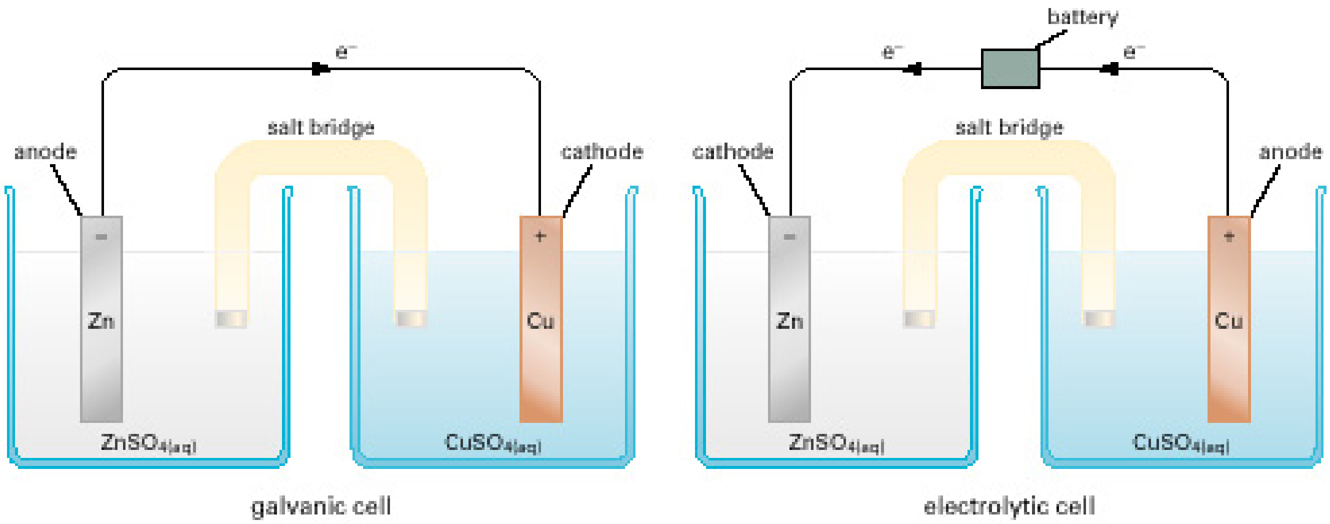

Figure 16.1 A galvanic cell VS an electrolytic cell

Table 16.1: Comparing Galvanic and Electrolytic Cells

GALVANIC CELL	ELECTROLYTIC CELL
Spontaneous reaction	Non-spontaneous reaction
Anode (negative): Zinc	Anode (positive): Copper
Cathode (positive): Copper	Cathode (negative): Zinc
Oxidation (at anode): $Zn \rightarrow Zn^{2+} + 2e^-$	Oxidation (at anode): $Cu \rightarrow Cu^{2+} + 2e^-$
Reduction (at cathode): $Cu^{2+} + 2e^- \rightarrow Cu$	Reduction (at cathode): $Zn^{2+} + 2e^- \rightarrow Zn$
Cell reaction: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$	Cell reaction: $Cu + Zn^{2+} \rightarrow Zn + Cu^{2+}$

Example 1:

The following reaction takes place in an electrolytic cell:

$Cu_{(s)} + Ni^{+2}_{(aq)} + \text{energy} \rightarrow Cu^{+2}_{(aq)} + Ni_{(s)}$

a) Write the oxidation and reduction half reactions
b) Show this reaction in shorthand notation

Solution 1:

As before assign oxidation numbers to each reactant and product,

$Cu_{(s)} + Ni^{+2}_{(aq)} + \text{energy} \rightarrow Cu^{+2}_{(aq)} + Ni_{(s)}$
0 +2 +2 0

Since the oxidation number of copper increases, it is undergoing oxidation.

Since the oxidation number of the nickel II ion decreases, it is undergoing reduction

$Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^-$ (oxidation)

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ (reduction)

Shorthand notation: $Cu_{(s)}\ |Cu^{2+}_{(aq)}\ ||\ Ni^{2+}_{(aq)}\ |\ Ni_{(s)}$

Support Questions

18. Explain the difference between a non-spontaneous and spontaneous reaction in terms of galvanic and electrolytic cells.

19. The following reaction takes place in an electrolytic cell:

    $Sn^{+2}_{(aq)} + 2Cl^-_{(aq)} + \text{energy} \rightarrow Sn_{(s)} + Cl_{2(g)}$

    a) Write the oxidation and reduction half-reactions
    b) Show this reaction in shorthand notation.

Applications of Electrolytic Cells

Electrolysis has many useful applications. Electrolysis of water produces oxygen and hydrogen gas by the following reaction:

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

The oxygen and hydrogen gas produced in electrolysis have many practical applications. Oxygen is a useful reactant for the production of pulp and paper, and it is also sold to patients with respiratory problems. Hydrogen is used to generate electricity to power electric buses and cars.

Electrolytic cells are also used (along with galvanic cells) to recharge batteries in a cellphone or a car.

Metal refining is another practical application of electrolytic cells. Many metals are not found in their pure elemental form in nature. Aluminum in nature is often found in a rock called bauxite. Bauxite mostly contains aluminum oxide, Al_2O_3. Electrolysis is used to isolate pure aluminum from bauxite. Aluminum has many practical applications such as boat and aircraft construction, pop cans, and construction materials to name a few.

Electroplating is a common practice that uses electrolysis and electrolytic cells. This is a method used when producing shiny fixtures in your home such as faucets, light fixtures, and doorknobs. Jewellery, cutlery, car/motorcycle fender and coins are also electroplated. During electroplating these objects are produced mostly from inexpensive metal such as steel. Electrolysis is used to add a thin layer of more expensive metal such as nickel on top. Figure 16.2 below depicts a spoon being coated with silver through the process of electroplating

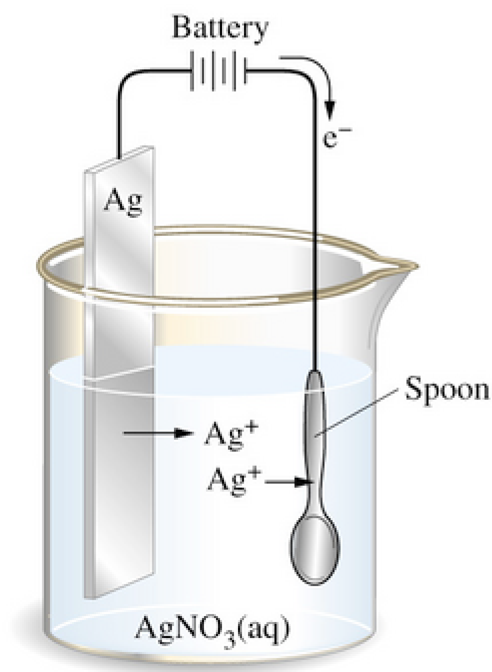

Figure 16.2 Electroplating a Spoon

In the diagram above, silver ions from the solution gain electrons and are reduced. The ions then solidify on the cathode, which is the spoon in this example. The solid silver anode loses electrons.

There are environmental drawbacks to electroplating. It consumes an incredible amount of electricity.

Most factories that manufacture products by electroplating are located near the water to produce electricity using water (hydroelectricity). However, most of the electricity generated in Ontario comes from the combustion of fossil fuels, which can produce carbon dioxide. You may recall from previous chemistry courses that excess carbon dioxide may lead to a greenhouse effect and acid rain. The process of electroplating can also cause cancer for workers exposed to the chemicals used in the process.

Faraday's Law

One of Michael Faraday's (1791-1867) major contributions to chemistry was the connection between stoichiometry and electrochemistry. This concept relates to the extraction and refining of many metals through electrolysis.

Faraday's Law: the amount of a substance produced or consumed in an electrolysis reaction is directly proportional to the quantity of electricity that flows through the circuit.

The charge on one mole of electrons is one Faraday = $\frac{96500\text{ C}}{1\text{ mol e}^-}$

RECALL

- the flow of electrons is called **electric current**, measured in **Amperes** (A)
- the quantity of electric charge, the **coulomb(C)** = current(A) x time(s)

Example 2:

Calculate the mass of aluminum produced by the electrolysis of molten aluminum chloride, if a current of 500mA passes for 1.50h.

Solution:

Given: electrolyte: $AlCl_{3(l)}$ current: $500mA \times \frac{1A}{1000mA} = 0.500A$

time: $1.5h \times \frac{3600s}{1h} = 5400s$

Required: $m_{\mathrm{Al}} = ?$

Equation(s): $\text{Quantity of Charge } (C) = \text{Current } (A) \times \text{Seconds } (s)$

$m = \eta \times M$

Solution:

$$
\begin{aligned}
C &= A \times s \\
&= 0.500A \times 5400s \\
&= 2700C
\end{aligned}
$$

$$
\begin{aligned}
\text{Amount of electrons} &= 2700C \times \frac{1\,mol\ \text{e}^-}{96500C} \\
&= 0.0280\ mol\ \text{e}^-
\end{aligned}
$$

$$\text{Al}^{3+} + 3\text{e}^- \Leftrightarrow \text{Al}$$

$$\frac{x\ mol\ \text{Al}}{0.0280mol\ \text{e}^-} = \frac{1\,mol\ \text{Al}}{3\ mol\ \text{e}^-}$$

$$
\begin{aligned}
x\ mol\ \text{Al} &= \frac{1\,mol\ \text{Al}}{3\ mol\ \text{e}^-} \times 0.0280mol\ \text{e}^- \\
&= 0.00933\ mol\ \text{Al}
\end{aligned}
$$

$$
\begin{aligned}
m &= \eta \times M \\
&= 0.00933\cancel{mol} \times 27.0\frac{g}{\cancel{mol}} \\
&= 0.252g
\end{aligned}
$$

Statement: The mass of aluminum produced is 0.252g.

Support Questions

20. What amount of electrons is transferred in a cell that operates for 1.25h at a current of 0.150A/mA?

Key Question #16

1. Describe two differences between a galvanic and an electrolytic cell. (4 marks)

2. Two half cells in a galvanic cell consist of one iron ($Fe_{(s)}$) electrode in a solution of iron (II) sulphate ($FeSO_{4(aq)}$) and a silver ($Ag_{(s)}$) electrode in a silver nitrate solution. (12 marks)

   a) Assume the cell is operating as a galvanic cell, state the overall and half-cell reactions. Describe what will happen to the mass of the cathode while the cell is operating.
   b) Repeat part a), assuming that the cell is operating as an electrolytic cell.

3. Calculate the mass of zinc plated onto the cathode of an electrolytic cell by a current of 750mA in 3.25h. (5 marks)

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Support Question Answers

Answers to Support Questions

Lesson 13

1. a) $Cu^{2+}_{(aq)} + \cancel{2Cl^-}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)} + \cancel{2Cl^-}_{(aq)}$

   $Cu^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

   Copper II is reduced
   Zinc is oxidized

   b) $2Ag_{(s)} + S_{(s)} \rightarrow Ag_2S_{(s)}$
   0 0 +2 -2
   silver is oxidized, sulphur is reduced

   c) $Cu^{2+}_{(aq)} + \cancel{SO_4^{2-}{}_{(aq)}} + Mg_{(s)} \rightarrow Cu_{(s)} + Mg^{2+}_{(aq)} + \cancel{SO_{4(aq)}}$

   $Cu^{2+}_{(aq)} + Mg_{(s)} \rightarrow Cu_{(s)} + Mg^{2+}_{(aq)}$

   Copper II is reduced
   Magnesium is oxidized

2. Ni = +2, Cl = -1

   Mg = 0

   Ti = +4, O = -2

   K = +1, O = -2, Cr = +6

   O = -2, S = +4

3. Assign oxidation numbers to the underlined atoms.

   a) Cl = +7
   b) Cr = +3
   c) Sn = +4
   d) Au = +3

4. a) $SnCl_4$, Sn = +4, Cl = -1
   b) MnO_4^-, Mn = +7, O = -2
   c) MnO_2, Mn = +4, O = -2

5. Mo = +4, S = -2

6. Which of the following equations represent REDOX reactions? Which do not represent REDOX reactions? Prove your answer with oxidation numbers

a) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
0 0 +1 -1

REDOX reaction occurs

b) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
+2+4 -2 +2 -2 +4 -2

Not a redox reaction

c) $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$
+1 -2 0 0

REDOX reaction occurs

d) $2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2LiOH_{(aq)} + H_{2(g)}$
0 +1 -2 +1-2+1 0

REDOX reaction occurs

e) $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$
+3 -2 +2 -2 0 +4 -2

REDOX reaction occurs

7. a) $4Al_{(s)} + 3MnO_{2(s)} \rightarrow 2Al_2O_{3(s)} + 3Mn_{(s)}$
b) $SO_{2(g)} + 2HNO_{2(aq)} \rightarrow H_2SO_{4(aq)} + 2NO_{(g)}$
c) $2HNO_{3(aq)} + 3H_2S_{(aq)} \rightarrow 2NO_{(g)} + 3S_{(s)} + 4H_2O_{(l)}$
d) $2Al_{(s)} + 3H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$

8. a) $Cr_2O_7^{2-}{}_{(aq)} + 6Cl^-{}_{(aq)} + 14H^+ \rightarrow 2Cr^{3+}{}_{(aq)} + 3Cl_{2(aq)} + 7H_2O_{(l)}$
b) $2MnO_4^-{}_{(aq)} + 3SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 3SO_4^{2-}{}_{(aq)} + 2MnO_{2(aq)} + 2OH^-{}_{(aq)}$

9. a) $2MnO_4^-{}_{(aq)} + Br^-{}_{(aq)} + 2H^+{}_{(aq)} \rightarrow 2MnO_{2(s)} + BrO_3^-{}_{(aq)} + H_2O_{(l)}$
b) $I_{2(s)} + 5OCl^-{}_{(aq)} + H_2O_{(l)} \rightarrow 2IO_3^-{}_{(aq)} + 5Cl^-{}_{(aq)} + 2H^+{}_{(aq)}$
c) $Cr_2O_7^{2-}{}_{(aq)} + 3C_2O_4^{2-}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 6CO_{2(g)} + 7H_2O_{(l)}$
d) $Mn_{(s)} + 2HNO_{3(aq)} + 2H^+{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

10. a) $2CrO_4^{2-}{}_{(aq)} + 3S^{2-}{}_{(aq)} + 8H_2O_{(l)} \rightarrow 2Cr(OH)_{3(s)} + 3S_{(s)} + 10\ OH^-{}_{(aq)}$
b) $2MnO_4^-{}_{(aq)} + I_{-(aq)} + H_2O_{(l)} \rightarrow 2MnO_{2(s)} + IO_3^-{}_{(aq)} + 2OH^-{}_{(aq)}$
c) $2H_2O_{2(aq)} + ClO_4^-{}_{(aq)} \rightarrow 2O_{2(g)} + ClO_2^-{}_{(aq)} + 2H_2O_{(l)}$
d) $S^{2-}{}_{(aq)} + 4I_{2(s)} + 8OH^-{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + 8I^-{}_{(aq)} + 4H_2O_{(l)}$

Lesson 14

11. a) Conductor – This is an aqueous ionic compound
    b) Non-conductor – Solid ionic compound (it is not ionized)
    c) Non-conductor – Pure distilled water has few/very few ions
    d) Non-conductor – Covalent compounds are non-conductors
    e) Conductors – Aqueous acids are conductors

12. Use the activity series to predict if a reaction will occur or not. If a reaction occurs, complete and balance your equation.

    a) $Zn_{(s)} + AgCl_{(aq)} \rightarrow Ag_{(s)} + ZnCl_{2(aq)}$
    b) $Cu_{(s)} + Sn(NO_3)_{2\ (aq)} \rightarrow$ no reaction
    c) $Mg_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_{2(g)}$
    d) $Ag_{(s)} + HNO_{3(aq)} \rightarrow$ no reaction
    e) $Zn_{(s)} + FeCO_{3(aq)} \rightarrow ZnCO_{3(aq)} + Fe_{(s)}$

Lesson 15

13. a) $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$ (oxidation)
    $Fe^{2+}{}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$ (reduction)

    b) $Zn_{(s)}\ |Zn^{2+}{}_{(aq)}\ ||\ Fe^{2+}{}_{(aq)}\ |\ Fe_{(s)}$

14. $E^o{}_{cell} = E^o{}_{red} + E^o{}_{ox}$
    $= 1.066V + (-0.536V)$
    $= 0.530V$

15. For the following cell, write the equation for the reactions occurring at the cathode and the anode and calculate the standard cell potential.

    $Sn\ |\ Sn^{2+}$ (1mol/L) || Cr^{2+} (1 mol/L) | Cr

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	-0.91

$E^o{}_{cell} = E^o{}_{red} + E^o{}_{ox}$
$= -0.91V + (0.14V)$ (change sign to write for oxidation)
$= -0.77V$

16. All cells have three basic parts: two electrodes (an anode and a cathode), and an electrolyte.

17. Dry cell batteries contain chemicals which are in a dry state, while wet cells contain acids which are in a liquid state.

Lesson 16

18. Galvanic cells contain a spontaneous reaction with electrons flowing from a higher potential to a lower potential, thereby generating electrical energy.

    Electrolytic cells use energy to move electrons from a lower potential energy to a higher potential energy. The overall reaction in an electrolytic cell is non-spontaneous, and requires an external source of energy to occur.

19. The following reaction takes places in an electrolytic cell:

    $Sn^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$ + energy $\rightarrow Sn_{(s)} + Cl_{2(g)}$

    a. Write the oxidation and reduction half-reactions

    $Sn^{+2}_{(aq)} + 2e- \rightarrow Sn_{(s)}$ (reduction)
    $2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$(oxidation)

    b. Show this reaction in shorthand notation.

    $Cl_{2(g)}$ $|2Cl^{-}_{(aq)}||$ $Sn^{2+}_{(aq)}$ $|Sn_{(s)}$

20.
$$\begin{aligned} t &= 1.25h \times 3600s/h \\ &= 4.5 \times 10^{3} s \end{aligned}$$

$$\begin{aligned} \eta_e &= \frac{0.150C/s \times 4.50 \times 10^{3} s}{9.65 \times 10^{4} C/mol} \\ &= 7.0 \times 10^{-3} mol \end{aligned}$$

Appendix A: Standard Cell Potentials

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Li^{+}(aq) + e^{-} \rightarrow Li(s)$	-3.04
$K^{+}(aq) + e^{-} \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^{-} \rightarrow Ca(s)$	-2.76
$Na^{+}(aq) + e^{-} \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$	-0.83
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$	-0.74
$Cr^{2+}(aq) + 2e^{-} \rightarrow Cr(s)$	-0.91
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^{-} \rightarrow Fe(s)$	-0.04
$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$	0.16
$ClO_4^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow ClO_3^{-}(aq) + 2OH^{-}(aq)$	0.17
$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$	0.22
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	0.34
$ClO_3^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow ClO_2^{-}(aq) + 2OH^{-}(aq)$	0.35
$IO^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow I^{-}(aq) + 2OH^{-}(aq)$	0.49
$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^{-} \rightarrow 2I^{-}(aq)$	0.54
$ClO_2^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow ClO^{-}(aq) + 2OH^{-}(aq)$	0.59
$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^{-} \rightarrow 2Hg(l)$	0.80

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^{-}$ -> $Hg(l)$	0.85
$ClO^{-}(aq) + H_2O(l) + 2e^{-} \rightarrow Cl^{-}(aq) + 2OH^{-}(aq)$	0.90
$2Hg^{2+}(aq) + 2e^{-} \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-} \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^{-} \rightarrow 2Br^{-}(aq)$	1.07
$O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$	1.36
$Ce^{4+}(aq) + e^{-} \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$	1.52
$H_2O_2(aq) + 2H^{+}(aq) + 2e^{-}$ -> $2H_2O(l)$	1.78
$Co^{3+}(aq) + e^{-}$ -> $Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^{-}$ -> $2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^{+}(aq) + 2e^{-}$ -> $O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^{-}$ -> $2F^{-}(aq)$	2.87

