

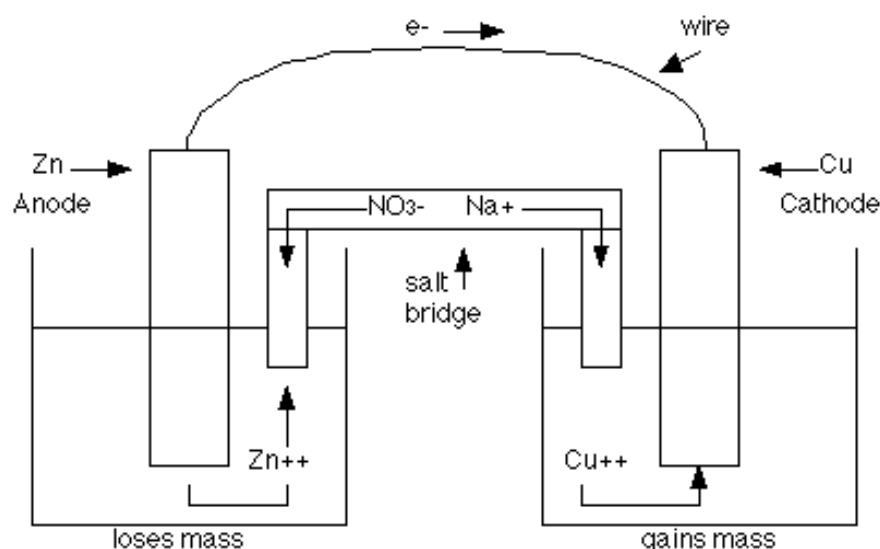
Redox Reactions & Electrochemistry

Oxidation and Reduction Reactions



The rusting of an old car. A burning campfire. A toy battery-operated car. The chemical processes in your body that break down carbohydrates to produce water, carbon dioxide and energy. The ripening of fruit.

It's not easy to see what all of these types of reactions have in common, but they all belong to a very important category of chemical reactions known as **oxidation - reduction, or redox, reactions.**



An electrochemical cell of the reaction:

$$\text{Zn(s)} + \text{Cu}^{++}(\text{aq}) \longrightarrow \text{Zn}^{++}(\text{aq}) + \text{Cu(s)}$$

1.1 Redox Reactions

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions.

The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion.

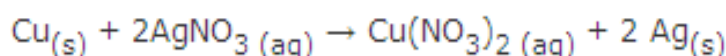
Reduction originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions an exchange of electrons occurs - one substance loses electrons while something else gains them. That is the key to understanding redox reactions. We'll define these terms below.

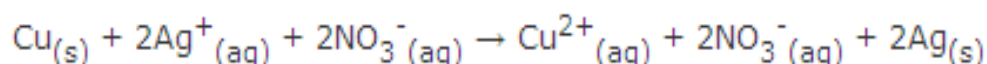
A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes the wire begins to look fuzzy or furry, as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint. Furthermore, if the crystals are shaken off of the wire we see that the wire partially disintegrated.



The overall equation for our demonstration describes the events:



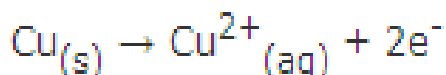
Remember that when we have aqueous solutions of ionic compounds, the ions are really present as separate ions, not as bonded particles. So we can write an expanded equation:



Removing the spectator ions gives us our **net ionic equation**:



Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

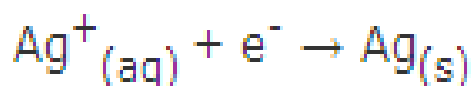


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Notice that copper began as a solid but is converted into aqueous ions - this is why the copper wire disintegrates.

We say that copper was **oxidized** because it has **lost electrons** (electrons appear on the product side of the equation).

Silver was converted from an ion with a charge of +1, Ag^+ , to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:



Notice that solid silver is formed - this is what causes the fuzzy appearance to begin appearing on the wire - solid silver crystals.

Silver has **gained electrons** - it has been **reduced**. (electrons appear on the reactant side of the equation.)

The electrons that silver gained had to come from somewhere - they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation - reduction reaction**.

Oxidation
the loss of electrons

Reduction
the gaining of electrons

LEO

the Lion
Says

GER



LEO

Loss of
Electrons
is Oxidation

GER

Gain of
Electrons
is Reduction

1.2 Oxidation Numbers

Redox reactions are all about electrons being transferred from one substance to another, so it would be useful if we had a system for keeping track of what gains and what loses electrons, and how many electrons are involved.

our record-keeping system is called **Oxidation Numbers**

Oxidation Numbers

A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons

ON Rules

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge.

2. Alkali metals - elements in the first column of the periodic table - will always have an oxidation number of +1; Alkali metals (column 2) are almost always +2

3. The oxidation number of hydrogen is almost always +1 when it is in a compound.

The oxidation number of oxygen is almost always -2 when it is in a compound

The exceptions:

4.
 - peroxides, such as hydrogen peroxide. In peroxides oxygen has an oxidation number of -1.
 - when oxygen is combined with fluorine it's oxidation number is +2

5. The sum of the oxidation numbers in a compound is zero.

6. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.

Element	Oxidation Number
---------	------------------

Na	
----	--

H ₂	
----------------	--

O ₂	
----------------	--

P ₄	
----------------	--

Ionic Compound	Oxidation Number
----------------	------------------

NaCl	
------	--

Mg ₃ N ₂	
--------------------------------	--

Compound	Oxidation Number
----------	------------------

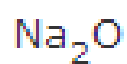
HCl	
-----	--

H ₂ S	
------------------	--

Compound	Oxidation Number
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magnesium oxide



sodium oxide



sodium peroxide

Compound

Oxidation
Number







Compound

Oxidation
Number

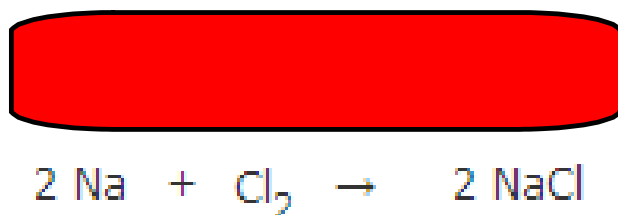


answers

Oxidation numbers are a convenient way of identifying redox reactions and also indicating which element is oxidized and which is reduced. Here's an example - the reaction between sodium metal and chlorine gas:



It is often useful to write the oxidation number for every element, in every compound, above the element in the equation. Thus for our reaction we have:



Be sure to note that the balancing coefficients in the equation (the "2" in front of Na and in front of NaCl) **do not** affect the value of the oxidation numbers. We'll return to these coefficients soon.

A chart is a useful way for us to summarize the changes in oxidation number for each element:

element	initial ox no	final ox no	change in electrons (e^-)	oxidized or reduced
---------	------------------	----------------	----------------------------------	------------------------

Na

Cl

Pull

We see several important things in our table -

- Since oxidation numbers did change, this **was** a redox reaction
- Na's oxidation number increased - from 0 on the reactant side to +1 on the product side. An element becomes more positive by *losing electrons*.

Loss of electrons is Oxidation (LEO)

- Cl's oxidation number decreased, from 0 to -1, as chlorine *gained electrons*.

Gain of electrons is Reduction (GER)



An increase in oxidation number indicates oxidation

A decrease in oxidation number indicates reduction

Consider the reaction



Determine oxidation numbers for all elements in every compound:



element	initial ox no	final ox no	change in electrons (e^-)	oxidized or reduced
---------	------------------	----------------	----------------------------------	------------------------

Two new terms before we continue. You will recall that we mentioned in the first section of this unit that oxidation cannot occur without reduction, and vice versa. The substance losing electrons (undergoing oxidation) gives its electrons to the substance gaining electrons (undergoing reduction). If the reduced substance will not accept electrons, the oxidized substance could not give away electrons. Thus, one allows for the other to occur.

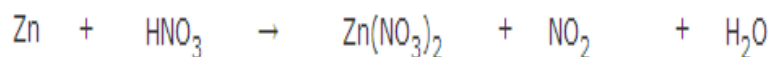
Reducing agent

the substance that is oxidized.
It allows another element to be reduced.

Oxidizing agent

the substance that is reduced.
It allows another element to be oxidized.

By convention we often refer to the oxidizing agent and reducing agents as the entire compound the element is in, not just individual element. Consider the following reaction. Oxidation numbers are shown only for substances whose oxidation numbers undergo a change:



Summarize:

element	initial ox no	final ox no	e ⁻	oxidized or reduced	Agent
<hr/>					

Here is a final example.

Consider the reaction



element	initial ox no	final ox no	e ⁻	oxidized or reduced	Agent
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answers



1.4 Balancing Redox Equations using Oxidation Numbers

In previous chemistry classes you learned how to balance equations. Following the Law of Conservation of Mass you learned that the number of atoms of each element must be the same on both the reactant and product side of the equation.

Many redox reactions cannot easily be balanced just by counting atoms. Consider the following net ionic equation:

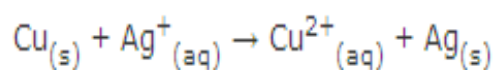


If you simply count atoms, the equation appears to be balanced

But do you see what *isn't* balanced - **the charges!**

on the reactant side of the equation you find a total charge of +1, versus +2 on the product side.

There are two common techniques we can use to help us balance redox reactions - the oxidation number method and the half-reaction method. We'll look at the oxidation number method first.

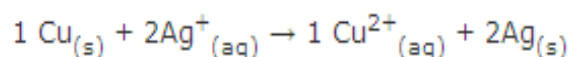
Balancing Equations using Oxidation Numbers

element	initial ox no	final ox no	change in e ⁻
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We can see that the number of electrons lost by copper does not equal the number gained by silver. We need to correct that, so we will multiply Ag by 2, giving us a total of two silvers. (We'll multiply copper by one - it won't change anything but will help keep us organized):

element	initial ox no	final ox no	change in e ⁻	balance for electrons
Cu	0	→ +2	lost 2	× 1 = 2
Ag	+1	→ 0	gain 1	× 2 = 2

The highlighted values - our multipliers to balance electrons - will become our balancing coefficients in the equation. Our chart helps us to keep organized and see that we should put a "1" in front of copper and a "2" in front of silver. Our balanced equation:



It is not necessary to put the "1" in front of copper.

Balance the following reaction using the oxidation number method:



element	initial ox no	final ox no	change in e^-	balance for electrons
---------	------------------	----------------	--------------------	-----------------------



Pull

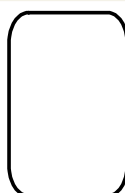
This example will show us another very important trick. Balance the following equation:



element	initial ox no	final ox no	change in e ⁻	balance for electrons
---------	------------------	----------------	-----------------------------	-----------------------



element	initial ox no	final ox no	change in e ⁻	No. atoms	No. e ⁻	balance for electrons
---------	------------------	----------------	-----------------------------	--------------	-----------------------	--------------------------



=
=



Balance:



element	initial ox no	final ox no	change in e^-	No. atoms	No. e^-	balance for electrons
---------	------------------	----------------	--------------------	--------------	--------------	-----------------------------

Pull

Pull

Pull

Practice



answers

1.5 Balancing Redox Equations using Half-reactions

Another way to balance redox reactions is by the half-reaction method. This technique involves breaking an equation into its two separate components - the oxidation reaction and the reduction reaction. Since neither oxidation nor reduction can actually occur without the other, we refer to the separate equations as **half-reactions**.

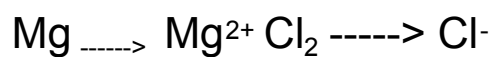
The general technique involves the following:

- The overall equation is broken down into **two** half-reactions. If there are any spectator ions, they are removed from the equations.
- Each half-reaction is balanced separately - first for atoms and then for charge. Electrons are added to one side of the equation or the other in order to balance charge. For example, if the reactant side of the equation has a total charge of +3, the product side must also equal +3.
- Next the two equations are compared to make sure electrons lost equal electrons gained. One of the half reactions will be an oxidation reaction, the other will be a reduction reaction.
- Finally the two half-reactions are added together, and any spectator ions that were removed are placed back into the equation

Consider the following reaction:



Record ON's



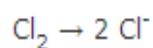
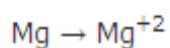
Balance the two reactions for atoms.



Next balance the equations for charge by adding electrons. Remember - one half-reaction will be an oxidation reaction (electrons on the product side) and the other will be reduction (electrons will be on the reactant side)

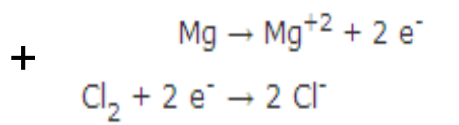
LEO

GER

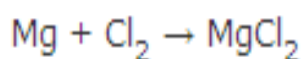


We then compare the two equations for numbers of electrons. We see that both equations have 2 electrons so we do not need to make any adjustments for that.

Finally, add the two equations together:



and reform any compounds broken apart in the earlier steps:



We see that the original equation was already balanced, not just for atoms but for electrons as well.

Next example:



Record ON's and identify the LEO H.R. and the GER H.R.

Pull

Write the balanced
half-reactions

Balance
electrons

Add half-reactions

Add equations together

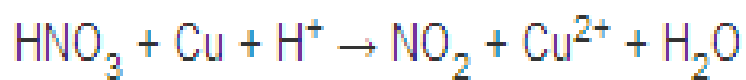
Reform compound/return spectator ions

Pull

Here is a reaction occurring in an acid solution, which accounts for the presence of the H^+ ions. This example adds a little more complexity to our problem.

Pull

Last example:



Pull

answers

Practice



Assignment



2.1 Introduction to Electrochemistry

During redox reactions, electrons pass from one substance to another. The flow of electrons - electric current - can be harnessed to do work. **Electrochemistry** is the branch of chemistry that deals with the conversion between chemical and electrical energy.

There are two major branches of electrochemistry, which we will examine in this section:

Electrochemical Cells	Electrolytic Cells
the energy released by a spontaneous chemical reaction is converted into electrical energy.	electrical energy is used to cause a non-spontaneous chemical reaction to occur.
Examples: batteries	Examples: recharging batteries & electroplating

2.2 Electrochemical Cells

The basic unit of all batteries is the electrochemical cell (also called a **voltaic cell** or **galvanic cell**). Electrochemical cells convert the energy of a spontaneous redox reaction into electricity. This will be accomplished as the electrons that are released from the oxidation half-reaction are passed to the reduction reaction which will absorb the electrons.

We will create an electrochemical cell based on the following redox reaction:



This reactions involves two half-reactions:



oxidation

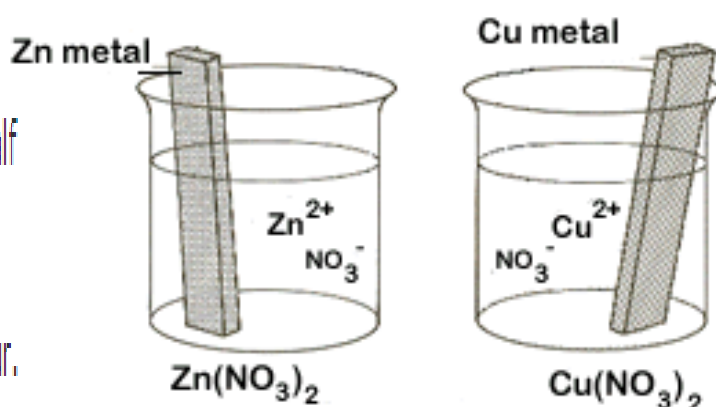


reduction

We'll walk through the set-up of our electrochemical cell:

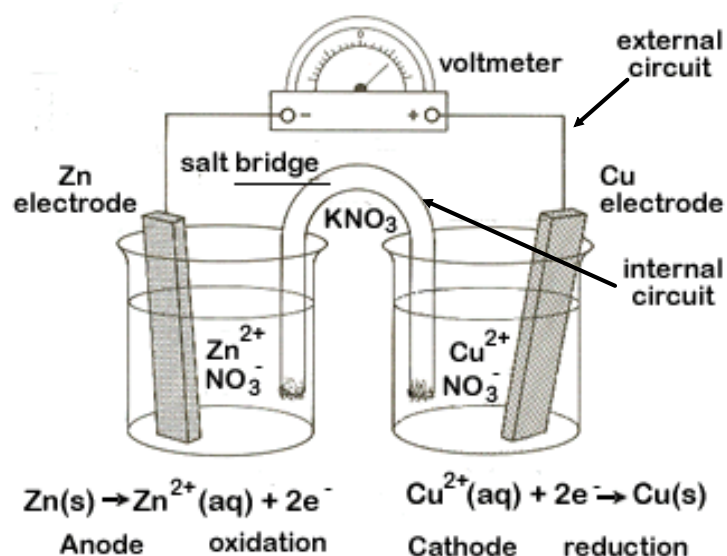
1. Begin by getting 2 beakers into which we will place metal strips in electrolytic solutions (solutions that conduct electricity due to the presence of ions). In one place a strip of zinc metal in a $\text{Zn}(\text{NO}_3)_2$ solution. In the other place a strip of copper metal in a $\text{Cu}(\text{NO}_3)_2$ solution.

Each beaker represents one of the two half cells. But because there is no way for electrons to move from one beaker to the other, our redox reaction cannot yet occur.



2. We need to connect our two half-cells which we need to do in two ways.

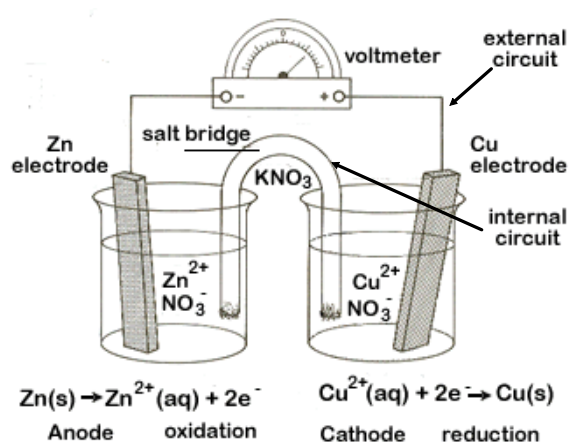
First we will connect the two metal strips, our **electrodes**, with some wire. We'll also place a voltmeter here so we can detect the electric current once we are up and running. This will be our **external circuit**.



Second we add a **salt bridge**. A salt bridge is a U-shaped tube that contains an electrolytic solution (we'll use KNO_3). This electrolytic solution will allow ions to flow between the two beakers. This is our **internal circuit**.

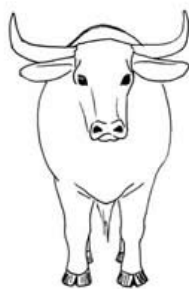
The zinc half-cell undergoes oxidation. Here, the solid zinc electrode disintegrates, forming zinc ions and releasing electrons. By definition, the half-reaction that undergoes oxidation in an electrochemical cell is called the **anode**.

The copper half-cell undergoes reduction. Here, copper ions from the electrolytic solution become deposited on the copper electrode, forming more solid copper. Electrons are required for this to occur. By definition, the half-reaction that undergoes reduction in electrochemical cells is called the **cathode**.

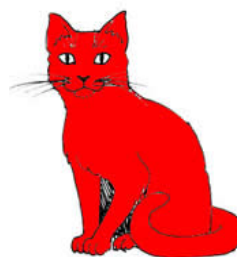


The anode is the source of electrons, making it the negative post of the electrochemical cell.

The cathode is the positive post of the electrochemical cell as it consumes electrons.



An Ox
Anode = Oxidation



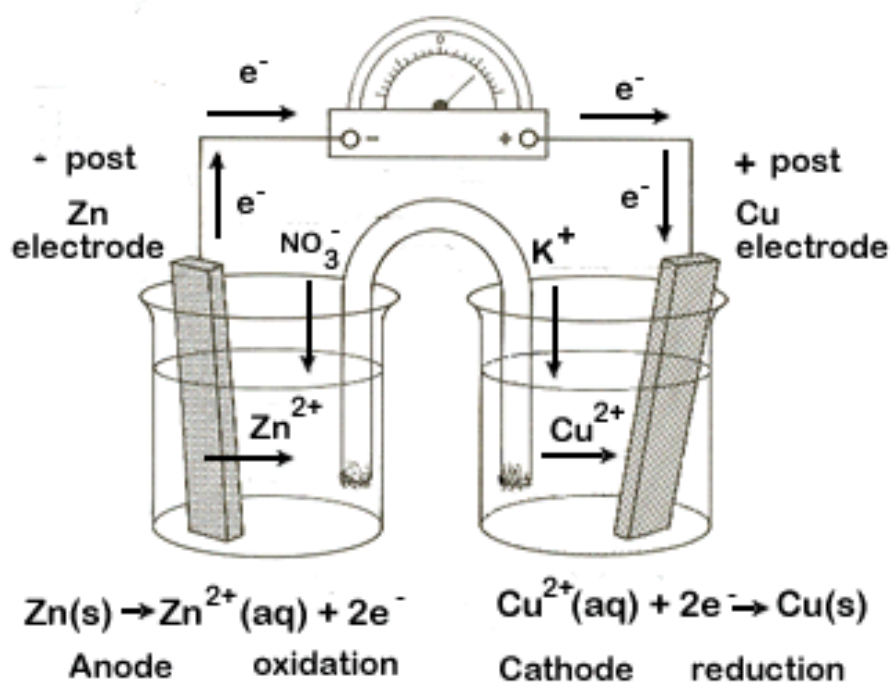
Red Cat
Reduction = Cathode

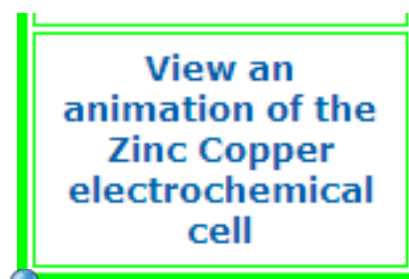
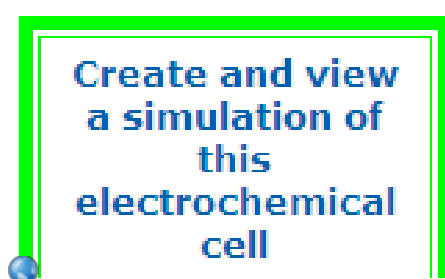
4. It is important to understand the roles of the external circuit and the salt bridge.

External circuit - this is where the electrical work is done as electrons travel from one half-cell to the other. The electrons are produced at the zinc anode, where oxidation occurs. The electrons then travel through the wire of the external circuit to the copper cathode. The electrons are then available for the copper ions (from the $\text{Cu}(\text{NO}_3)_2$ solution) and solid copper is produced.

Internal circuit -

At the anode, Zn^{2+} ions are being produced and go into solution. This causes a build-up of positive ions in this solution. If this electrical imbalance is not corrected the reaction cannot continue. The excess positive charge attracts the negative NO_3^- ions (anions) from the salt bridge, thereby keeping the solution electrically neutral.





At the cathode the opposite occurs. As positive Cu^{2+} ions are removed from solution, to form solid Cu, the solution becomes overly negative. This attracts the positive K^{+} cations from the salt bridge, keeping this side of the cell neutral.

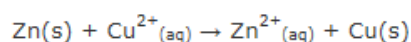
External Circuit	Internal Circuit
Electrons flow from A to C	Anions to the Anode
Anode to Cathode	Cations to the Cathode

Let's build an electrochemical cell!

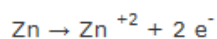


2.4 Calculating Voltages of Electrochemical Cells

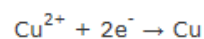
Let's return to our zinc - copper electrochemical cell. We can now use the **Table of Standard Reduction Potentials** to not only calculate the voltage of our cell, but also to explain why it was zinc, and not copper, that underwent oxidation.



This reactions involves two half-reactions:



oxidation

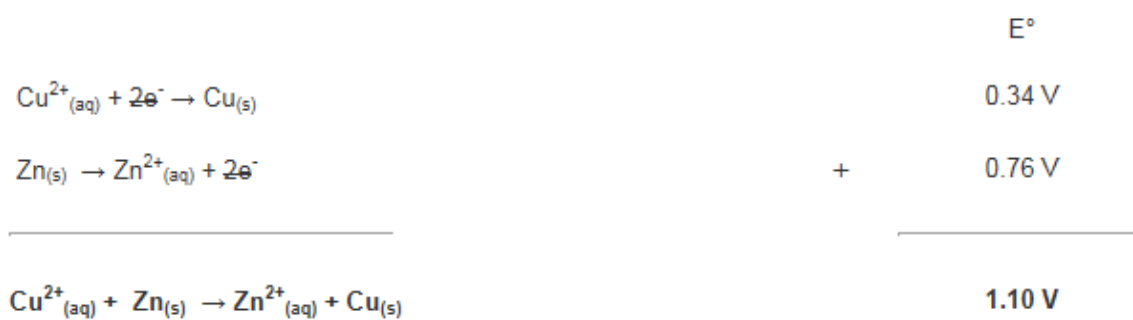


reduction

Before calculating the voltage of a cell you must first determine which half-cell will undergo oxidation and which one will be reduced. Find the copper and zinc half-reactions in the Table of Standard Reduction Potentials. Be careful - there is often more than one half-reaction for an element. For copper locate the $\text{Cu}|\text{Cu}^{2+}$ half-reaction (unless otherwise directed, always use this half-reaction for copper).

	E°
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Cu}_{(\text{s})}$	0.34 V
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Zn}_{(\text{s})}$	-0.76 V

In the Table, all reactions are written as reduction reactions. The E° values indicate which half-reaction is better at competing for electrons. Since the copper half-reaction has a larger value for E° than the zinc half-reaction, copper will be reduced, forcing zinc to be oxidized. So we reverse the zinc equation and in doing so change the sign for zinc. As long as electrons cancel out, we can then add the two equations together to get the full redox reaction and determine the voltage of the cell:



Pull

A positive value of E° indicates a spontaneous chemical reaction

Electrochemical cells always involve a spontaneous chemical reaction

Let's try one more example of setting up an electrochemical cell.

We want to create an electrochemical cell using **aluminum** ($\text{Al}|\text{Al}^{3+}$) and lead ($\text{Pb}|\text{Pb}^{2+}$) half-cells. Our tasks:

1. Determine the two half-reactions involved, and which reaction will undergo oxidation and which one will be reduced.
2. Determine the voltage of the cell.
3. Diagram the set-up of the electrochemical cell, including the following items:
 - the two half-cells, including the electrodes and electrolytic solutions
 - the external circuit, showing the direction of electron flow
 - the salt bridge with an electrolyte, including movement of ions
 - label the anode and the cathode
 - label the positive and negative posts

Step 1

Before you begin to create your diagram you need to determine what will be oxidized and what will be reduced. At the same time you can calculate the voltage of the cell. Locating the two half-reactions in the Table of Standard Electrode Potentials:

Pull

Step 2

Since lead has a larger electrode potential than does aluminum, lead will be reduced and aluminum will be oxidized. So we will reverse the aluminum equation and **reverse its sign**.

Also identify what is oxidized and what is reduced.

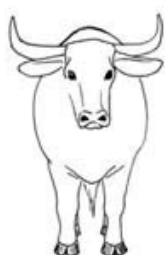
Pull

Step 3

We can now calculate the cell voltage. A useful tip - you know if you've switched the correct equation when you get a positive voltage. **All electrochemical cells will have a positive voltage!**

Another key thing to know - this is new. We must balance the two equations for electrons before we add them together. However, **this will NOT change the value of E° !!!**

Pull

Step 4

At this time we will also determine which electrode will be the anode and which will be the cathode.
Remember - **An Ox and a Red Cat:**



Pull

Step 5

Now that we have all of the key information we can diagram the cell.

Step-by-step:

1. Draw 2 beakers, each containing an electrode - the two metals used in our reactions. To each beaker add an electrolytic solution. The electrolyte will include the metal ion and another ion (NO_3^- is usually a good choice since it will not form a precipitate).
2. Add an external circuit (the wire connecting the two electrodes) and a salt bridge with an electrolytic solution (KNO_3 is often a good choice).

Pull

3. Indicate the following on your diagram:

- Direction of electron flow (Electrons flow from A to C)
- Ion movement from the salt bridge (Anions to Anode; Cations to Cathode)
- Positive and negative posts (the anode - site of oxidation - releases electrons so it is the negative post; the cathode - site of reduction - uses up electrons so it is the positive post).

Pull



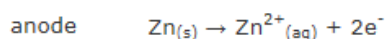
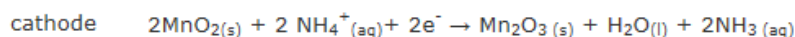
answers

2.6 Batteries

Electrochemical cells used for power generation are called batteries. Although batteries come in many different shapes and sizes there are a few basic types. You won't be required to remember details of the batteries, but some general information and features of each type is presented here.

1. Primary batteries - (dry cell batteries)

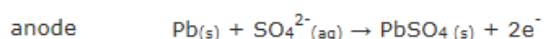
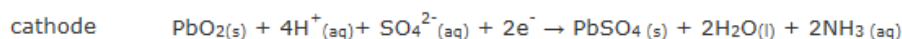
- non-rechargeable
- electrolytes are present as a paste rather than as a liquid
- general purpose battery used for flashlights, transistor radios, toys, etc.
- The basic dry cell battery consists of: zinc case as the anode (oxidation); a graphite rod is the cathode (reduction) surrounded by a moist paste of either MnO_2 , NH_4Cl , and ZnCl_2 or in alkaline dry cells a KOH electrolytic paste.
- General reactions for the battery - manganese(IV) oxide-zinc cell (different batteries have different reactions - you don't need to remember any of these reactions)



- Maximum voltage 1.5V. By connecting several cells in series 90V can be achieved.
- Advantages of alkaline batteries - consistent voltage, increased capacity, longer shelf-life, and reliable operation at temperatures as low as -40°C
- Disadvantage - higher cost

2. Secondary Batteries (storage batteries)

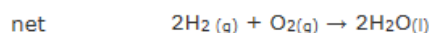
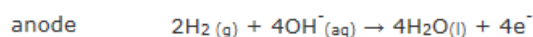
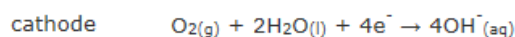
- rechargeable
- an example - lead-acid battery used in cars. Anode is grid of lead-antimony or lead-calcium alloy packed with spongy lead; Cathode is lead(IV) oxide. Electrolyte is aqueous sulfuric acid. Consists of numerous small cells connected in parallel (anode to anode; cathode to cathode).
- General reaction:



- Secondary batteries are recharged by passing a current through the battery in the opposite direction. In a car battery this occurs when the engine is running.
- Other examples include the nickel-iron alkaline battery, nickel-zinc battery, nickel-cadmium alkaline battery, silver-zinc, silver-cadmium

3. Fuel Cells

- fuel cells are electrochemical cells that convert energy of a redox combustion reaction directly into electrical energy. Requires a continuous supply of reactants and a constant removal of products.
- Cathode reactant usually air or pure oxygen; anode fuel is a gas such as hydrogen, methane, or propane. Carbon electrodes typically contain a catalyst. The electrolyte is typically KOH .
- General reaction:

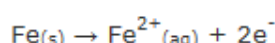


- Advantages - no toxic waste products (water is the only product); very efficient energy conversion (70-80% efficient)
- Disadvantage - too expensive for large-scale use.

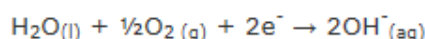
2.7 Corrosion of Metals

Corrosion of metals is a serious economic problem. Corrosion occurs as a result of the spontaneous electrochemical reaction, as the metal undergoes oxidation.

For example, the rusting of iron begins with the oxidation of solid iron:



The corresponding reduction reaction involves water:



The flaky brown solid we call rust forms when Fe^{2+} undergoes additional oxidation to form Fe^{3+} , then reacts with hydroxide ions to form iron(III) oxide, Fe_2O_3 , and iron(III) hydroxide, $\text{Fe}(\text{OH})_3$.

The rate of corrosion can be affected by several factors. Some examples . . .

- Metals corrode faster when in contact with another metal. The Statue of Liberty, for example, has a skin made of copper but is supported by iron ribs. Since iron is oxidized more readily than copper, it acts as the anode. Earlier repairs to strengthen the stature used iron bolts which exacerbated the problem. More recent repairs has replace the iron ribs with stainless steel alloys. Stainless steel resists corrosion.
- Salt water speeds up the corrosion process because the ions in salt water form a salt bridge between the anodic and cathodic sites. Salt may be great for icy roads, but it is tougher on cars.

There are a number of ways to slow down corrosion, if not prevent it.

- Prevent oxygen and water from contacting the metal. This can be accomplished by paint, grease, plastic, or other methods of covering the metal.
- Cathodic protection - pieces of zinc or magnesium metal may be bolted to the surface of iron. Both Zn and Mg are oxidized more readily than Fe, which results in those metals being oxidized thus sparing and protecting the iron. Propeller shafts of speedboats are often protected this way. Anode rods in water heaters also work this way (they are often called "sacrificial anodes"). Galvanized nails - nails coated with the more reactive zinc - provide yet another example.
- Metal alloys - an alloy is a mixture of metals, or a mixture of a nonmetal with a metal. An alloy such as stainless steel (chromium is added to steel - a mixture of iron and other elements such as carbon - to make stainless steel) is highly resistant to corrosion but can be prohibitively expensive.

3.1 Introduction to Electrolysis

Think of electrolysis and electrolytic cells as the opposite of electrochemical cells:

	Electrochemical Cells	Electrolytic Cells
Energy conversion	Chemical → Electrical	Electrical → Chemical
Spontaneous chemical reaction?	Yes	No
Value of E°	Positive	Negative

In an electrochemical cell, a spontaneous redox reaction is used to create an electric current; in an electrolytic cell the reverse will occur - an electric current will be required in order to cause a non-spontaneous chemical reaction to occur.

We will look at three examples of the electrolytic process, keeping our discussion on a very basic level - the electrolysis of molten sodium chloride, the electrolysis of water, and electroplating.

3.2 Electrolysis of Molten Sodium Chloride

If we look at the latin roots of the word "electrolysis" we learn that it means, essentially, to "break apart" (*lysis*) using electricity.

Our first example of electrolytic cell will examine how an electric current can be used to break apart an ionic compound into its elements.

The following equation represents the breaking apart of $\text{NaCl}_{(l)}$:



The half-reactions involved in this process are:

		E°
reduction	$2\text{Na}^+_{(l)} + 2\text{e}^- \rightarrow \text{Na}_{(s)}$	-2.71 V
oxidation	$\text{Cl}^-_{(l)} \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$	-1.36V
net voltage required		- 4.07V

Notice that a negative voltage (-4.07V) results when we add up the half-reactions. This tells us that the overall reaction will **NOT** be spontaneous, and a minimum of 4.07 volts will be required for this reaction to occur.

As we shall see, our set-up will have a number of similarities to our electrochemical cells. We will need electrodes and an electrolyte to carry the electric current.

Some key differences with an electrochemical cell set-up:

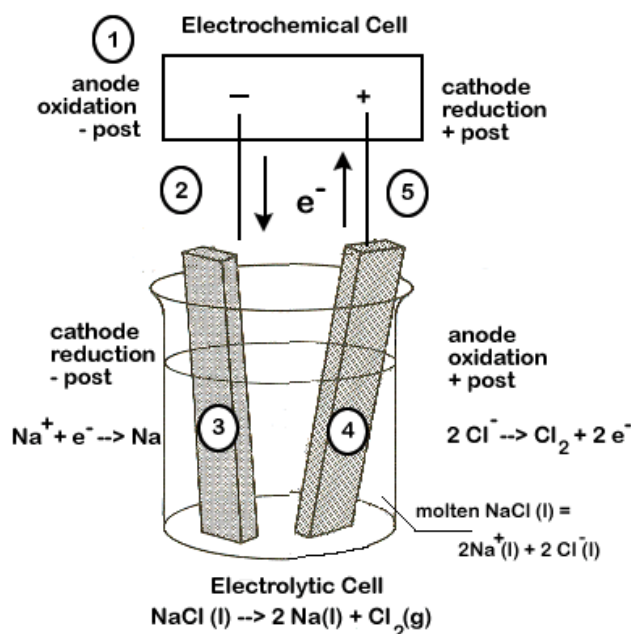
- the two half-reactions are not separated by a salt bridge
- an electrochemical cell (or other source of electric current) will be required

Other important items to note:

- The anode of the electrolytic cell is the site of oxidation and the cathode is the site of reduction, just as in an electrochemical cell.
- In an electrochemical cell, the anode is negative and cathode positive, but this is reversed in the electrolytic cell - the anode is positive and the cathode is negative.

Carefully study the diagram of our set-up, taking special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

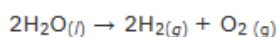
1. Electrons are "produced" in the battery at the anode, the site of oxidation.
2. The electrons leave the electrochemical cell through the external circuit.
3. These negative electrons create a negative electrode in the electrolytic cell which attracts the positive Na^+ ions in the electrolyte. Na^+ ions combine with the free electrons and become reduced ($2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$)
4. Meanwhile the negative Cl^- become attracted to the positive electrode of the electrolytic cell. At this electrode chlorine is oxidized, releasing electrons ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$)
5. These electrons travel through the external circuit, returning to the electrochemical cell.



3.3 Electrolysis of Water

Our second example of electrolysis and electrolytic cells involves the breakdown of water. We will find a situation very similar to the electrolysis of molten NaCl.

The following equation represents the breaking apart of $\text{H}_2\text{O}(l)$:



It may be more difficult to predict the half-reactions involved, but they are:

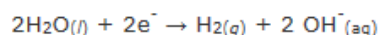
		E°
reduction	$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83 V
oxidation	$2\text{H}_2\text{O}(l) \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$	-1.23V
(see note below for net equation)		
net voltage required		- 2.06V

The set-up will be very similar to our last example with some minor differences. Water does not carry a charge well, so an electrolyte is added to the water. Vinegar, a weak acid (acetic acid) may be used. To collect the hydrogen and oxygen gases produced, inverted test tubes are often added, as shown in our diagram below.

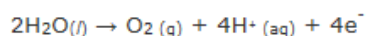
Again, take special care to trace the path of the electrons. Unless electrons make a complete circuit, a reaction will not occur.

1. Electrons are "produced" in the battery at the anode, the site of oxidation.
2. The electrons leave the electrochemical cell through the external circuit.
3. These negative electrons create a negative electrode in the electrolytic cell which causes the reduction of water.

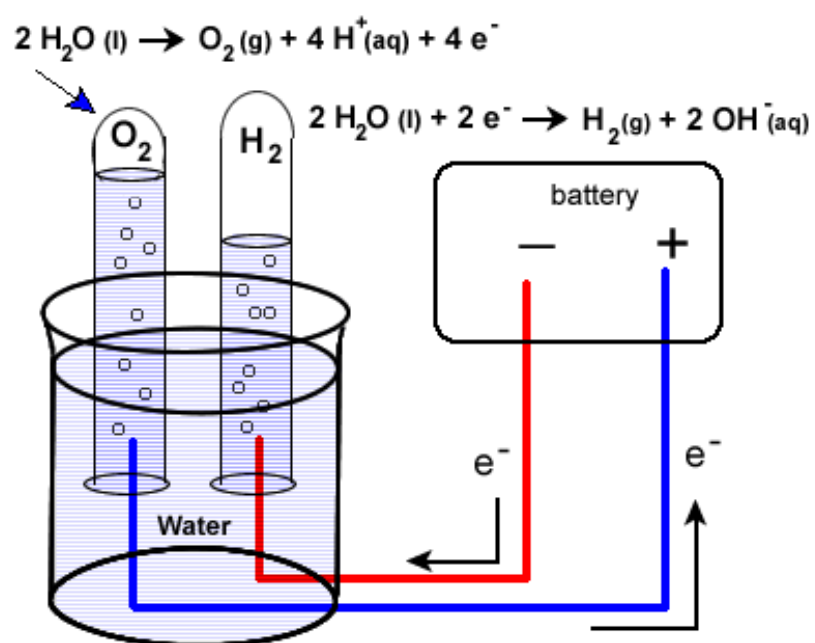
Note that the area around this electrode will become basic as OH^- ions are produced.



4. Meanwhile the the positive electrode water will undergo oxidation:



5. Electrons produced during this oxidation process will return to the electrochemical cell.



3.4 Electroplating

Our final example of electrolytic cells will examine a technique in which the electrodes actively participate in the reaction, instead of merely just carrying the electrical charge.

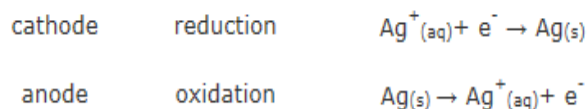
Electroplating is a technique in which a thin layer of a desired metal is used to coat (or "plate") another object. This process is often used to protect objects against corrosion or to improve their appearance.

For our example we will exam the silver plating of flatware. In our example we will coat a fork made with an inexpensive metal with a thin layer of silver.

As with our other electrolytic cells we have three requirements:

- an electrolytic solution. Our electrolytic solution will need to contain ions of the plating metal. We will use AgNO_3 which will give us our required Ag^+ ions.
- a source of current (an electrochemical cell - a battery), and
- two electrodes. One of our electrodes will be the object to be coated (the fork), while the other must be the plating metal (a bar of silver).

Our half-reactions will be a bit different this time - both will involve the same reaction:

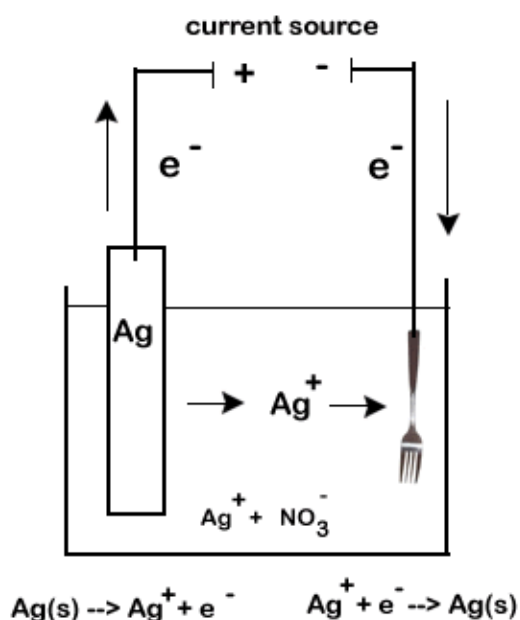


Here's the overall plan of action:

- We want solid silver to be deposited on the fork. Thus the fork electrode must be the cathode, or site of reduction. Positive silver ions from the electrolytic solution will be attracted to a negative electrode causing the deposition of solid silver.
- The Ag^+ will come from the electrolytic solution. As they get used up, they will need to be replaced.
- The silver bar will be the source of new Ag^+ . The bar will act as the anode and undergo oxidation. As it disintegrates it produces new Ag^+ .

The final concern is to account for the flow of electrons. Remember, our electrolytic cell will be hooked up to a battery (a set of electrochemical cells) or other source of current.

- Electrons will leave the negative post of the battery (the anode).
- These electrons will travel through the external circuit to the cathode of the electrolytic cell (our fork, the cathode)
- The anode of the electrolytic cell produces more electrons as it undergoes oxidation. These electrons return to the current source.



answers