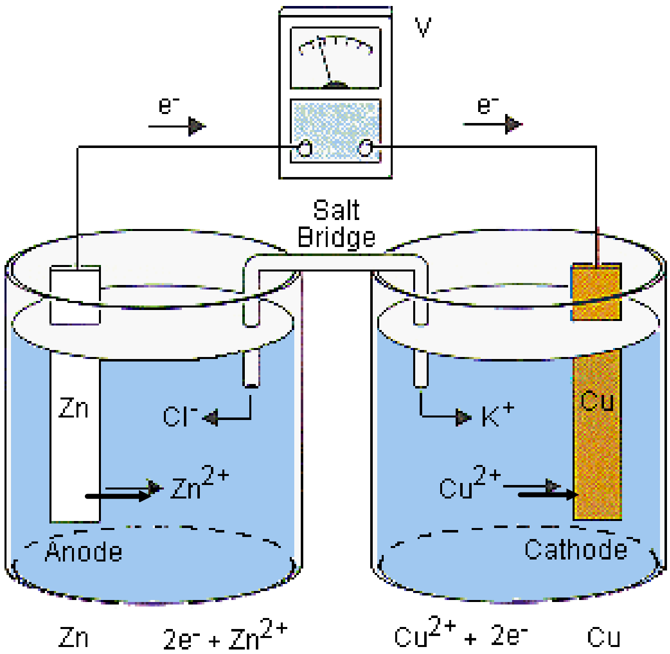
7.4 - Introduction to Electrochemistry and Calculating Voltages

pages 633-642 in Heath



During a redox reaction, electrons are passed from one substance to another.

- We call the flow of electrons **electric current**. This current can be harnessed to do work.

Electrochemistry is the branch of chemistry that deals with the conversion between chemical and electrical energy.

An **electrochemical cell** is the basic unit of a battery. It converts energy from a spontaneous redox reaction into electricity (from the flow of electrons through a metal or ion movement in a solution).

- This transformation from chemical energy to electricity will happen as the electrons are passed to from one substance to another in a redox reaction.

For example, an electrochemical cell can be made by using the following reaction:

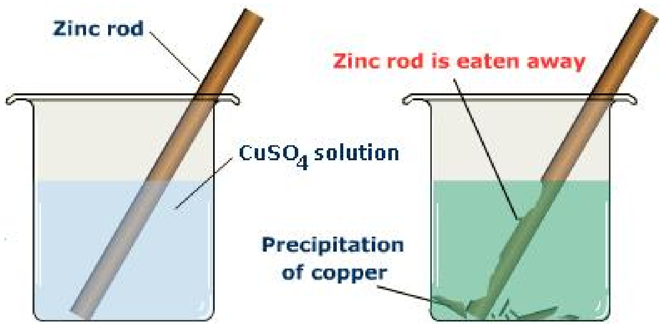
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

This reaction involves the two half reactions:

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

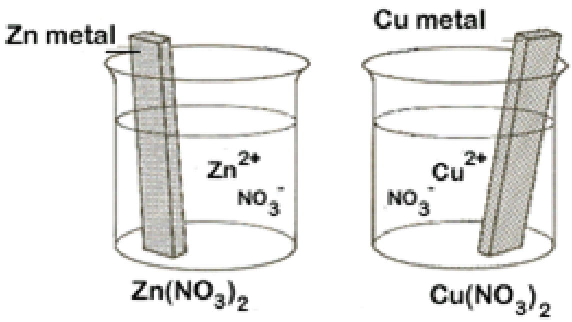
oxidation reduction

To create electricity, we must have our electrons pass through an **external circuit**. If we simply placed Zn in Cu^{2+} ions a reaction would occur, but electricity would not be created.



Here is how an electrochemical cell can be created with this reaction:

1. We need two beakers containing *electrolytic solutions*. One beaker will contain $Zn(NO_3)_2$ and the other will contain $Cu(NO_3)_2$. Zn metal will be placed in the first beaker while Cu metal will be in the second (these are called the **electrodes; electrically conducting solids which are placed in contact with electrolyte solutions**).

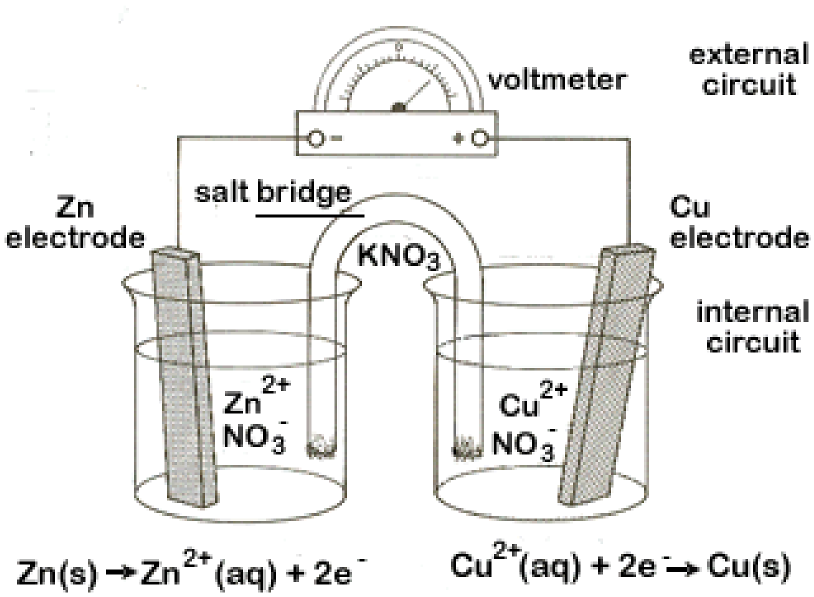


Since the electrons cannot move between the substances yet our redox reaction cannot occur yet. Therefore each beaker contains half a cell.

2. The two half cells must be connected in two ways.

First we must connect our electrodes with wire. Connected to the wire should be a voltmeter (a device that detects electric current). This is known as the **external circuit**.

Second we add a **salt bridge**, which is a U-shaped tube that also contains an electrolytic solution (KNO_3 in this case). This solution will allow electrons to flow freely between the two beakers. This is known as the **internal circuit**.



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

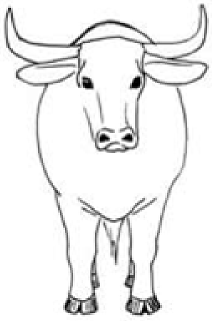
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ Cathode reduction

3. In the Zn half cell, the Zn electrode will disintegrate which forms Zn^{2+} ions and releases electrons. Therefore oxidation occurs here.

The half cell that undergoes oxidation is called the **anode**. This is the producer of electrons making it the negative post.

A mnemonic:

'An Ox' Anode = Oxidation

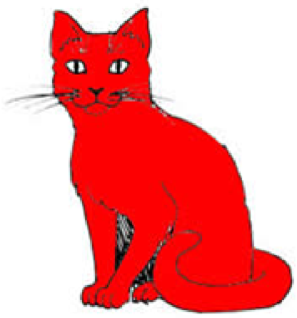


Conversely, the Cu half of the cell the Cu electrode gets Cu deposited on it. This requires electrons. Therefore, reduction is happening here.

The half cell that undergoes reduction is called the **cathode**. This is the positive post of the cell as it consumes electrons.

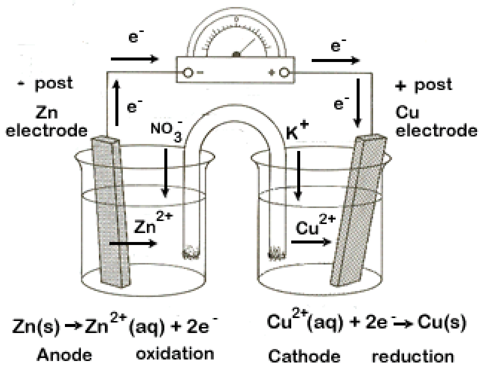
A mnemonic:

'red cat' reduction = cathode



The external circuit is where all the electrical work is done as the electrons flow from the anode to the cathode.

The internal circuit is used to keep each half cell electrically neutral.



If the anode's half cell is producing Zn^{2+} then it will attract the NO_3^- from the salt bridge.

Likewise, if Cu^{2+} is leaving the anode's solution then it will attract the K^+ from the bridge.

Therefore, **electrons flow from the anode to the cathode.**

- Anions flow to the anode side of the cell.
- Cations flow to the cathode side of the cell.

At this point, the cell is complete and electrons can flow allowing the redox reaction to proceed.

When the mass of each electrode is measured before and after the reaction, it is found to be different. The copper electrode will have a greater mass after the experiment and the zinc electrode will have less mass.

Standard Electrode Potentials

Why was Zn oxidized and Cu reduced in the hypothetical electrochemical cell we made last section? The answer is due to **valence electrons.**

Metals, in the first place, only have a few valence electrons which means they like to get rid of them (become oxidized).

However, metals differ in how easily they can lose their electrons. A list of how easily a metal can lose its electrons is known as the **activity series**. *The higher the metal is on the chart, the more likely it is to lose electrons (become oxidized).*

Table 20

Metal Activity Series

Metal	Metal Ion	Reactivity
Lithium	Li+	Most Reactive
Potassium	K+	-
Calcium	Ca2+	-
Sodium	Na+	-
Magnesium	Mg2+	-
Aluminum	Al3+	-
Manganese	Mn2+	-
Zinc	Zn2+	-
Chromium	Cr2+, Cr3+	-
Iron	Fe2+, Fe3+	-
Lead	Pb2+	-
Copper	Cu2+	-
Mercury	Hg2+	-
Silver	Ag+	-
Platinum	Pt2+	-
Gold	Au+, Au3+	Least Reactive

This difference in ability to lose electrons is what drives electrochemical cells and it is the force that allows electrons to flow from the anode to the cathode.

- This force is known as **potential difference** or **electromotive force (emf or E)**.

Potential difference is measured in **volts (V)** and will be referred to as **voltage**. This is a measure of the tendency of electrons to flow through the external circuit.

The higher the voltage the greater the tendency for electrons to flow from the anode to the cathode. That is, more current is produced with a higher voltage.

Calculating Voltages

The voltage for electrochemical cells can be found using a **standard electrode potential for half reaction** table *(Table 18 and 19)*. Note that the table may have more than one half reaction for a given element. Therefore, pay close attention to the specific **ion** listed.

The standard reduction potential of a half-cell is a measure of the tendency to GAIN electrons; higher number = greater oxidizing agent.

Chemists have decided to use the hydrogen half-cell as the standard to which all other half-cell potentials will be compared. The hydrogen half-cell potential is written as $E^{o} = 0.00V$ (E^{o} = 1 M solutions are standard temp and pressure)

The table shows the voltage for a number of half reactions. Notice that the half reactions listed are all **reduction** reactions.

If we know the substances of two half cells we can use the table to determine which will be the anode (oxidation) and which will be the cathode (reduction). You will need to change the sign of the given E^{o} value for the oxidation reaction.

When we know this, we can calculate the voltage of the electrochemical cell adn determine if the reaction is spontaneous.

****If the total E^{o} is positive, your redox reaction is spontaneous in the forward direction.**

****If the total E^{o} is negative, your redox reaction is spontaneous in the reverse direction.**

Ex: An electrochemical cell is produced from the following two half-cells: (Pb^{2+} | $Pb_{(s)}$) and ($Al_{(s)}$ | Al^{3+})

a. Determine E^{o}

b. Identify the anode and the cathode

c. State whether the forward reaction will be spontaneous.

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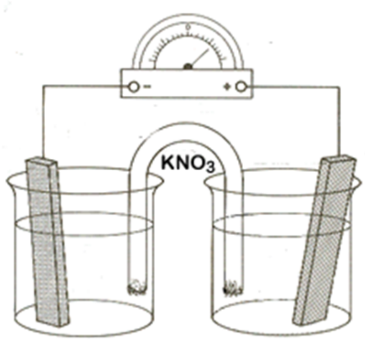
Steps to calculate voltage:

1. Write down the half reactions.
2. Determine which is the anode and which is the cathode. The reaction with the largest voltage will be the cathode since it will be reduced. Write down the voltage associated with the cathode.
3. Write down the voltage associated with the anode. We will need to switch the sign on this value as it is being oxidized instead of reduced.
4. Get the same number of electrons in each half reaction and add the two half reactions together. This allows us to cancel out our electrons and find the overall full redox reaction and the voltage.

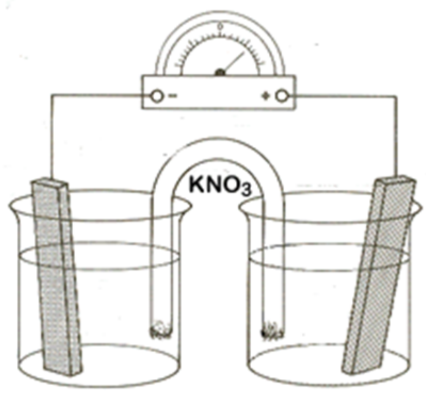
Ex) Calculate the voltage for the following electrochemical cells and label the following items on the diagrams for each:

i) A cathode and the substance it is made of
ii) An anode and the substance it is made of
iii) The correct half reaction under each beaker
iv) The ions coming off or attaching to each electrode
v) The direction of the ions in the salt bridge
vi) The direction of the flow of electrons

a) copper-copper(II) and zinc-zinc(II) half cell.



b) (Al | Al^{3+}) and (Pb|Pb^{2+})



7.4 Electrochemistry Worksheet

1. Calculate the voltage produced for each of the electrochemical cells containing the substances below. On each diagram, label:

   i. A cathode and the substance it is made of

   ii. An anode and the substance it is made of

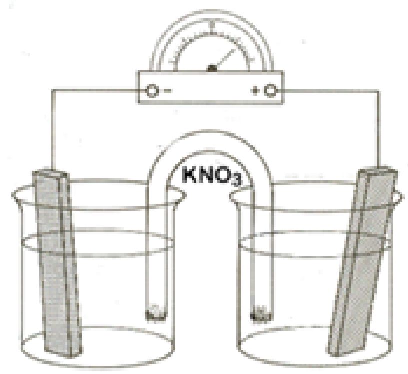
   iii. The correct half reaction under each beaker

   iv. The ions coming off or attaching to each electrode

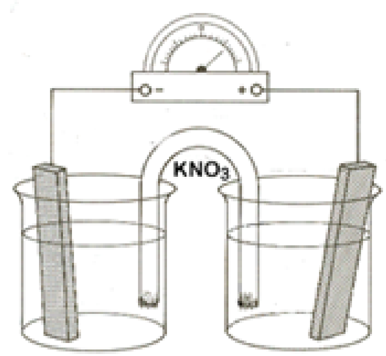
   v. The direction of the ions in the salt bridge

   vi. The direction of the flow of electrons

a) ($Fe|Fe^{2+}$) and ($Pb|Pb^{2+}$)



b) ($Cr|Cr^{3+}$) and ($Li|Li^{+}$)



2. Determine the E° for a (Ag | Ag^+) and (Zn|Zn^{2+}) electrochemical cell

3. Determine E° for a $Fe_{(s)}$ | $Fe^{2+}_{(aq)}$||$Cu_{(s)}$|$Cu^{2+}_{(aq)}$

4. a) An electrochemical cell is created using gold and magnesium half-cells. Write the redox reaction. Determine which half-cell will undergo oxidation and which will undergo reduction, identify which substance is the anode and cathode, and calculate the voltage for the cell. You do not need to draw a diagram of the cell.

b. If the mass of the magnesium electrode changes by 5.0 g, what will be the change in mass of the gold electrode, and will its mass increase or decrease? (hint – use mole to mole stoichiometry using the redox equation found in part a)