

## RedOx Pt 2

### Electrochemical Cells (AKA simple batteries)

An electrochemical cell has 3 major components:

1. The Cathode (and it's corresponding solution)
2. The Anode (and it's corresponding solution)
3. The salt bridge (allows for migration of charged ions)

There's also got to be a wire, but that's kind of taken for granted.

Let's look at a simple, functioning electrochemical cell for Copper and Zinc.  $\text{Cu}/\text{Cu}^{2+}$  and  $\text{Zn}/\text{Zn}^{2+}$

The CATHODE is the electrode (metal part) where CATIONS migrate to, it is GAINING electrons, and therefore undergoing REDUCTION.

The ANODE is the electrode (metal part) where ANIONS migrate to, it is LOSING electrons, and therefore undergoing OXIDATION.

Another mnemonic:

**An Ox CaRed** (Anode: Oxidation / Cathode: Reduction) or...

*Red Cat* (that's just for one electrode, but you must be pretty smart to have come this far, so I think you can figure out the other one by process of elimination)

Every electrochemical cell has to have two things happening:

1. Electrons moving from ANODE to CATHODE (alpha)
2. Ions migrating, this one's easy to forget, so DON'T!

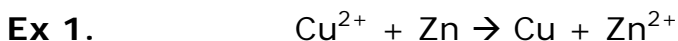
**HW Hebden pg 217, #34 and #35**

## Reactions in Electrochemical Cells

Electrons in Electrochemical cells move through external wires from the ANODE to the CATHODE (Alphabetical)

The strength with which each oxidizing agent in each half-cell attracts electrons and undergoes reduction is its *half-cell reduction potential* denoted as  $E^\circ$

The difference in reduction potentials between the two half-cells is the *electrochemical cell potential* and is measured in volts (V) It is this difference in reduction potentials that drives the electrons towards the half-cell with the greater reduction potential (stronger oxidizing agent)



The cell voltage is then a measure of how readily electrons move from one half-cell through the wires to another half-cell.

## Half-Cell Potentials

If one of the two half-cells in a RedOx reaction is a reference half-cell of known electric potential, then the measured electrochemical cell voltage will allow calculation of the other half-cells' reduction potential.

The standard reference half-cell is the hydrogen half cell (chosen arbitrarily, but it's simplistic) and is given the reduction potential of 0.00V

**Ex 1.** An electrochemical cell consisting of a copper half-cell and a hydrogen half-cell has a measured cell potential of 0.34 V. What is the reduction potential of the copper half-cell?

**Ex 2.** An electrochemical cell consisting of a zinc half cell and a hydrogen half cell has a measured cell potential of 0.76 V. The zinc electrode is losing mass, what's the reduction potential of the zinc-half cell?

Multiplying a half cell by some whole number coefficient DOES NOT change the reduction potential!

**Ex 3.** What voltage is produced by an electrochemical cell consisting of  $\text{Ag}/\text{Ag}^+$  and  $\text{Cu}/\text{Cu}^{2+}$ ?

**HW Hebden pg 224-226 # 38, 40-42**

## Spontaneity of RedOx reactions

RedOx reactions with a positive cell potential will proceed as written: they are *spontaneous*. If the cell potential is negative, the no forward reaction (reverse is preferred) can write N.R.

**Ex 1.** Will a gold ring dissolve in 1M HNO<sub>3</sub> to form Au<sup>3+</sup>?

**Ex 2.** Is Fe<sup>3+</sup> going to react with I<sup>-</sup>?  
(From the solubility unit does it react in a double replacement style?)

**Ex 3.** What (if anything) occurs when Cu wire is placed in 1M AgNO<sub>3</sub>?

## Types of Batteries

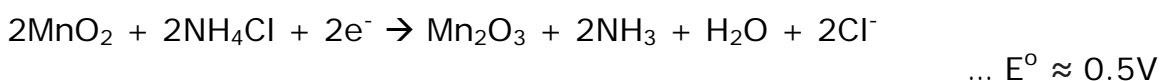
### Zinc Carbon Dry Cell (and later Zinc-Chloride cell)

First developed around 1890's and then refined. See demo cut in half.

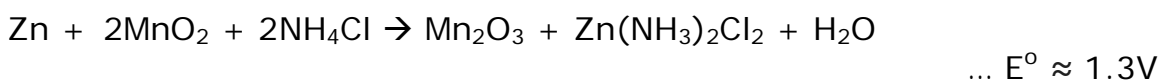
Anode:



Cathode:



Overall Reaction:

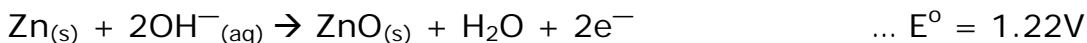


Has a graphite (C) rod surrounded by manganese powder as the positive terminal (cathode). The above could be better termed the zinc-manganese cell, but that never took off. The zinc-chloride cell uses a  $\text{ZnCl}_2$  paste rather than an  $\text{NH}_4\text{Cl}$  electrolyte mixture. The Zn/Cl system is simpler, longer lasting and steadier voltage output.

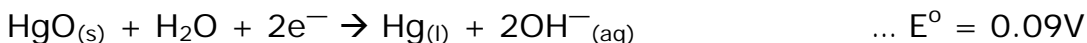
### Mercury Battery

One of the first small batteries made for commercial use (~1940's)

Anode:



Cathode:



Overall Reaction:

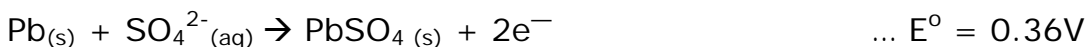


Electrolyte use is a concentrated KOH solution held in pads of absorbent material between the two electrodes

## Lead Storage Battery

This is still mainly the common battery used to start a car and run accessories off of. It is made of a number of electrochemical cells, each having a voltage of about 2V. These cells are connected in series so that their voltages are additive. Most car batteries are 12V batteries, meaning they have 6 cells.

Anode (Made of several plates of lead metal):



Cathode (Made of several plates of lead oxide):



Overall Reaction:



Electrolyte use is sulphuric acid, which is why sulphuric acid is commonly called "battery acid". As the reaction proceeds the sulphuric acid gets used up, this changes the density of the electrolyte, so an easy way to check the state of your car battery is to check the density of your battery. Of course the battery "remakes" sulphuric acid as you charge it, usually with the cars alternator.

## Hydrogen Fuel Cell

Another invention for having portable power: someone could make hydrogen (gas or liquid) at home by using electrolysis (next section) use that as fuel, and react with the oxygen in the air. The combustion of hydrogen and oxygen would work the same way as with the current combustion engine, with one major difference the product of the combustion is only water.

## Electrolysis (The Electrolytic Cell)

We can force non-spontaneous electrochemical reactions to occur by applying the necessary voltage. An electrolytic cell is a device that allows for electrolysis to occur.

### Simple Case: Molten cells

When we take molten (heated up to melting point) salts, and pass a current with sufficient voltage to force the usually non-spontaneous reaction to occur we can force the more stable forms (ions) of these elements into their less stable elemental forms. Once melted the ions are mobile, so no salt bridge is required. They simply migrate towards the electrode required

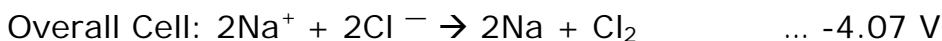
Ex.  $\text{NaCl}_{(l)}$  - Inert Electrodes (C or Pt, maybe Au) are used.

\*\* In actuality the cell is much more complicated than this, due to logistical problems of  $\text{Na}_{(s)}$  and  $\text{Cl}_{2(g)}$  mixing they must be separated.

The Cathode reaction (where cations migrate):



The Anode reaction (where anions migrate):



The overall reaction requires 4.07V (minimum) for the cell to operate. However the actual cell may require much more voltage in practice due to internal resistance of the cell.

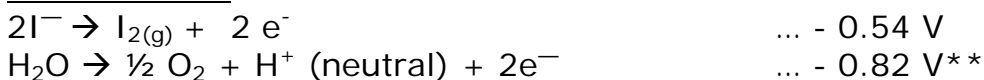
## Aqueous Electrolytic Cells

Problems arise when we have to take water into account. Now we have to consider another species that may or may not take place in the reaction (depends on reduction potentials)

Ex.  $\text{KI}_{(\text{aq})}$  - again electrodes made of inert substances

So we have to look at all possible reactions and their voltages.

At the Anode:



At the Cathode:



We chose the reactions that require less voltage – or HAVE A GREATER TENDANCY TO REDUCE/OXIDIZE (respectively)

**\*\*Overpotential effect:** In reality, aqueous electrolytic cells require MORE voltage to obtain water/hydrogen/oxygen than you would expect given their standard reduction potentials from electrochemical cells (The reason for this is a thermodynamic argument that is covered in university level physical chemistry)

For now, simply *use the standard potential on the chart for electrochemical cells, and the overpotential effect for electrolytic cells.* We will only worry about this for water/aqueous solutions (even though there are a lot more in real life)



Ex. What products will be produced at which electrodes with electrolysis of an aqueous solution of  $\text{ZnSO}_4$ ?

Cathode:

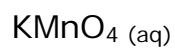
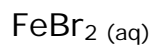
Anode:

Ex. What is a good choice of salt to use if I want to produce hydrogen and oxygen via electrolysis of water (P.S. I'd rather not poison my students)

Cathode:

Anode:

Ex. What is the minimum voltage required and what products would form at each electrode with the following solutions:



**HW. Hebden Pg 237-242 #64-70**

# Applied Electrolytic Cells

## Electroplating

Plating of one metal onto another to make it more attractive, resistant to corrosion, or just because it's cool

Cathode – object to be plated (ex. Key, dime)

Plating solution – ions that will be plated onto cathode

Anode – sacrificial metal to be *plated* onto the cathode

Ex. Copper plating of a key

## Electrorefining

Refining of a mixture of metals to remove impurities. (ex. pig copper)

Cathode – Pure metal that you want to obtain (ex. Cu)

Plating solution – ions of metal, same as cathode but ionic (ex.  $\text{Cu}^{2+}$ )

Anode – impure metal to be purified. Any metals that are LESSER OA's (Ex. Zn, Pb) will be oxidized into ions. Any metals that are GREATER OA's (Ex. Au, Ag) will not be oxidized and will remain on the anode!

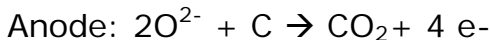
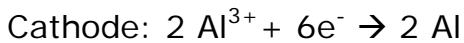
Ex. Refinement of pig copper

## Electro-winning - purification of ore

Sometimes you have impurities that are NOT other metals, but non-metals. These are usually found in rocks, and are called ORE.

Ex. Bauxite ore = mostly  $\text{Al}_2\text{O}_3$

After initial purification we're left with  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  - hydrated aluminum oxide, the water is driven off via heating. Molten  $\text{Al}_2\text{O}_3$  is then purified to using electrolysis to produce Aluminum metal via:



The anode, made of carbon, will react with the  $\text{O}^{2-}$  floating around in solution, and will need to be replaced.

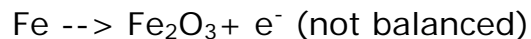
Requires a massive amount of energy (~300 MJ) so a lot of Al production actually happens around hydro plants in BC (Kitamat)

Make sure you RECYCLE (~10 MJ)

**HW from Hebden: Pages 244-246 #'s 73-80**

## Corrosion, and its prevention

Corrosion is an all-encompassing term meaning a gradual destruction of a metal, usually through oxidation and via environmental factors. Corrosion turns a solid metal (that can be used for structures and tools) into a salt of the metal ion. The most common form of corrosion is Rust:



Other types of corrosion

Copper corrosion - see statue of liberty

Aluminum corrosion - all Al foil you usually see, the "dull side" is  $\text{Al}_2\text{O}_3$

Silver corrosion - often called "tarnish"

Etc...

What conditions will help RUST to form on steel/iron?

Ideal conditions for rust formation include but are not limited to:

- A) Wet, or in a moist atmosphere --> water is required for conduction of charge and movement of e-
- B) Surrounded by oxygen, oxygen is a strong OA (readily available)
- C) If there is dissolved salt that helps, allows for increased conduction of charge

Rusting is a multi-step reaction involving Fe, water and oxygen:

1.  $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+} + 2e^{-}$
2.  $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^{-} \rightarrow 2\text{OH}^{-}$
3.  $\text{Fe}(\text{OH})_2 \rightarrow \rightarrow \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$  <--lots of steps

To go from  $\text{Fe}(\text{OH})_2$  to  $\text{Fe}_2\text{O}_3$  requires many steps that you don't really need to know. The "X" just means some number of water, usually between 0-10, this variation accounts for the different colours of rust

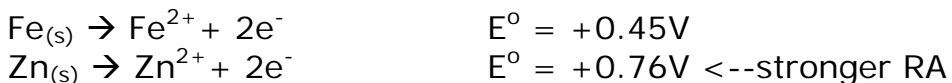
## Preventing Corrosion

2 main ways to prevent corrosion

1. Coat metal in something so that it won't get wet/oxidized, such as:
  - Plastic or Paint
  - Another metal that won't corrode as easily, or at all - Ag, Au, PtThere are many industrial applications of this, and ways of doing it. Think about all the metal things you have, most are painted or covered in plastic - Cars

2. Cathodic protection

Have the main metal (iron/steel) in contact with a metal that oxidizes easier, such as zinc. Could even just be in contact with a small part of the metal you're protecting



Electrons that could be lost from Fe come from Zn instead because the two metals are in constant contact and are conductive. Fe effectively acts like a "wire" and not the anode.

Galvanization: Zinc coating of a metal - this uses BOTH methods from above: coating, and cathodic protection.

Can also make mixtures of metals such as alloys that won't corrode:  
Ex. Stainless steel.