

XVII) Electrolysis & Electroplating

April 30, 2018 8:40 PM

XVII) Electrolysis

Recall that a spontaneous cell (a battery) is called an electroCHEMical cell.

What is an electrolytic cell?

- non-spontaneous rxn (redox)
- battery is required to "force" e^- flow in the reverse direction.

How does an electrolytic cell function?

The battery drives the e^- from anode to cathode, but for the NON-spontaneous rxn.

What is **electrolysis**?

a non-spontaneous redox rxn, which requires a power supply (such as a battery)

Why don't electrolytic cells need separate half-cells?

The reactants CAN be in direct contact b/c the rxn is non-spontaneous and will NOT OCCUR until an external power source is provided.

There are two types of electrolytic cells.

1. Molten Electrolytic Cell - NO H_2O !
2. Aqueous Electrolytic Cell - H_2O present

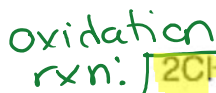
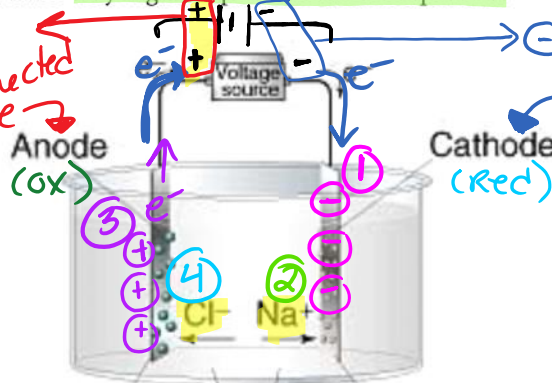
1) Molten Electrolytic Cell- Electrolysis of a **Molten (Liquid) Salt**

A molten salt is a salt that has been melted into liquid form, so no water is present in the cell. This takes very high temperatures and is expensive.

~~H₂O~~

(+) side of battery (cathode) always connected to the anode electrode

(only ions of salt.)
(-) side of the battery (anode) always connected to the cathode electrode



bubbles @ anode

Molten NaCl

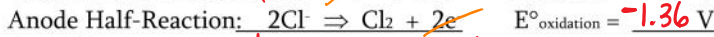
The only substances in the cell available to react are Na⁺ and Cl⁻.

(non-spont)

The spontaneous rxn. would involve Cl₂(g) + Na(s)

The electrodes are **inert**, meaning they are **unreactive**.

1. The inert cathode electrode becomes negatively charged as the battery pumps electrons to it.
2. The negative charge draws Na⁺ ions to the cathode to be reduced.
3. The inert anode electrode becomes positively charged because the battery pulls electrons away from it.
4. The positive charge draws Cl⁻ ions to the anode to be oxidized.

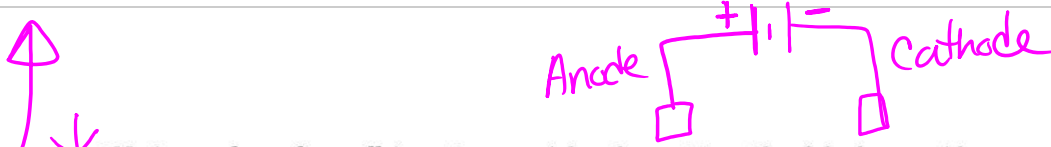


(+1.36 flip sign of oxidation)

↑ ⊖ non-spontaneous

(Slightly) more than 4.07 V would have to be supplied by the battery in order to make this cell function.

To "force" a non-spontaneous rxn you must apply more than the E°_{cell} .



*Notice on the molten cell (previous page) that the positive side of the battery (the cathode) is always connected to the anode of the electrolytic cell. The negative side of the battery (the anode) is always connected to the cathode of the electrolytic cell.

Sometimes, when solving a problem, this is the only hint you're given in order to determine the anode and cathode of the electrolytic cell.

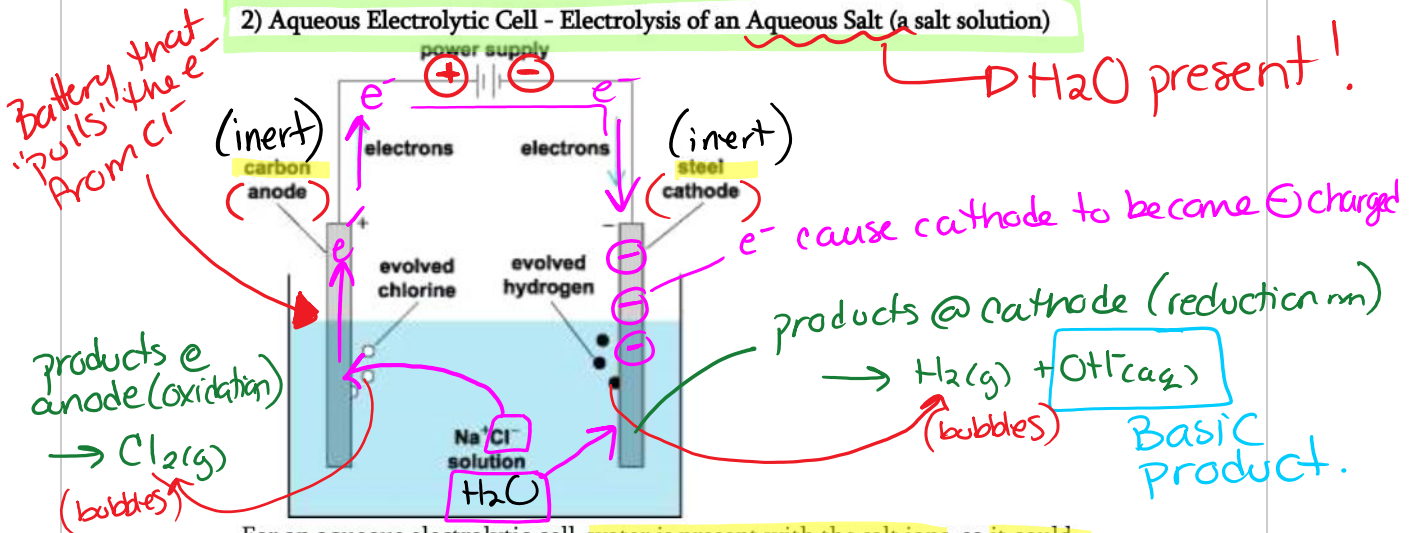
2) Aqueous Electrolytic Cell - Electrolysis of an Aqueous Salt (a salt solution)



H₂(l) present!

norm. we e-

2) Aqueous Electrolytic Cell - Electrolysis of an Aqueous Salt (a salt solution)



For an aqueous electrolytic cell, water is present with the salt ions, so it could oxidize or reduce in place of the ions (depends on half-reactions on the table). Use the table to determine the half-reactions.

will not be reduced (below the "over potential" of H₂O) (Red) (ox)

Potential O.A.	Potential R.A.
Na ⁺	Cl ⁻
H ₂ O	H ₂ O

will be oxidized (below the "over potential" of H₂O)

Cathode Half-Reaction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$ Voltage = -0.41 V

Anode Half-Reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ Voltage = -1.36 V ← (flip sign)



The battery must provide a voltage of slightly more than +1.77 V.

What colour would the solution be if phenolphthalein was added? Why?

PINK (basic) pH > 9.1
OH⁻ ions are produced in the reduction of H₂O (∴ basic sol'n/environment)

Practice Questions:

1. Draw a diagram for, find the half-reactions, overall reaction, and voltage necessary to run an $MgCl_2$ cell.

no H_2O present (molten cell)

$Cl_2(g)$ produced.

product is $Mg(s)$ metal

Cathode: $Mg^{2+} + 2e^- \rightarrow Mg(s)$ $E^\circ(V) = -2.37V$

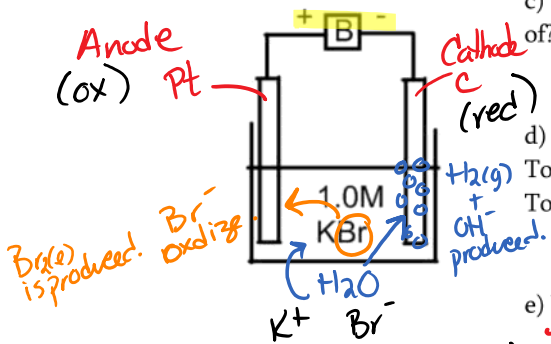
Anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$ $-1.36V$

Net Redox: $Mg^{2+}(l) + 2Cl^-(l) \rightarrow Mg(s) + Cl_2(g)$ $E^\circ_{cell} = -3.73V$

\therefore Battery needs to be slightly more than $+3.73V$ to force non-spontaneous rxn.

2. Consider the following cell:

- a) Is this cell molten or aqueous?
1.0M solution
- b) Which side is the anode?
left
- c) What are the anode and cathode composed of?
inert electrodes (C, Pt, Au, steel)



- d) Which substances are competing ...
- To reduce?
- To oxidize?

O.A	R.A
K^+	Br^-
H_2O	H_2O

- e) What is the 'overpotential effect'?
water reduces/oxidizes "out of order" when in (aq) solution

(ox) Anode: $2Br^- \rightarrow Br_2(l) + 2e^-$ $E^\circ(V) = -1.09V$

(red) Cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ $-0.41V$

f) Write the half-reactions and overall reaction (with voltages).

Net: $2Br^-(aq) + 2H_2O(l) \rightarrow Br_2(l) + H_2(g) + 2OH^-(aq)$

$E^\circ_{cell} = -1.50V$

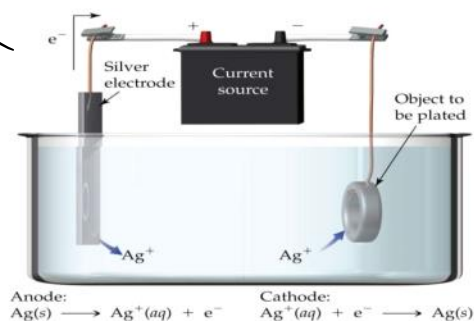
g) what observations could you make for the cathode?
bubbles due to production of $H_2(g)$.

3. Draw an electrolytic cell capable of electrolyzing water (water is oxidized and reduced) to make H_2 and O_2 . Ions must be present in the cell (to maintain cell neutrality at each electrode), so a salt must be part of the cell. Give the half-reactions and the overall reaction (including voltages).

Assignment 16: Do Hebden p.238 #64ab & p.242 #65abc, 67, 69, 71

Electroplating

Electroplating is an electrolytic process where a metal is plated onto another metal for protection or decoration.



The metal that will be used for plating is first oxidized at the anode (from metal to ion). It then travels across the electrolyte as a cation (it's attracted to the electrons waiting at the cathode) and is reduced at the cathode (from ion back to metal).

What is the overall reaction of the electroplating cell above?

What is the point of electroplating if there is no overall reaction?

For an electroplating cell, what is the anode and what is the cathode?

What should the electrolyte be composed of?

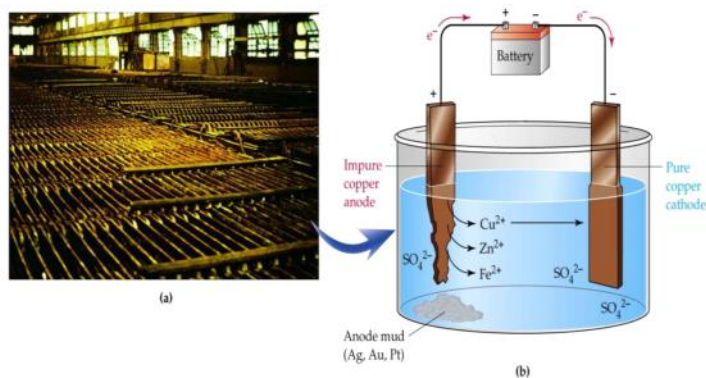
What voltage must be supplied by the battery in order for the electroplating to occur?

Design an electrolytic cell which will result in a *nickel coin being plated with copper*. Label the anode, cathode, and electrolyte. Give the half-reactions, the overall reaction, the voltage, and the voltage required for the process to occur.

Design an electrolytic cell which could be used to *electroplate an iron hood ornament with chromium*. Draw the cell and label all parts. Show the direction of electron flow in wire. Write the half-reactions and identify a suitable electrolyte.

Electrorefining

An electrolytic process where impure metal ore becomes pure metal. Below is an example of electrorefining copper.



The impure copper ore anode contains various amounts of zinc, iron, silver, platinum, and gold, but mostly copper. What order will these metals oxidize?

Because copper will always be on the surface of the anode (since the anode is *mostly* copper), silver, platinum, and gold will never get a chance to oxidize and will fall to the bottom of the cell making the 'anode mud'. Therefore, when zinc is on the surface of the ore, it will oxidize. When it isn't, Fe will oxidize. And when neither is on the surface, copper will oxidize.

Therefore, what three cations will exist in the solution?

What ion out of the three listed is best at reducing?

Therefore, why will Cu^{2+} be the only ion to reduce onto the pure Cu cathode?

Once all of the copper is reduced, the cell is terminated. The electrolyte is $\text{CuSO}_4(\text{aq})$, in order to have extra Cu^{2+} ions in solution.

Assignment 17:

- 1) Do Hebden p.244 #73,75,76
- 2) Read p.245-246 and do #77

You JUST finished your LAST unit of High School Chemistry!