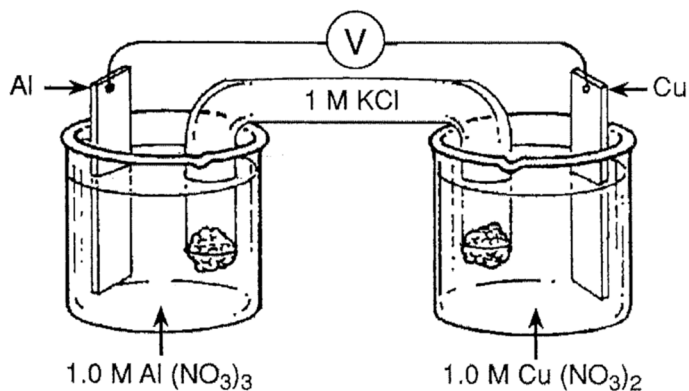


Unit 5 - Electrochemistry

General Principles

- Electrochemistry is the chemistry associated chemical energy being converted into electricity and vice versa.
- For the average person this translates into processes involved in electrical cells, more commonly known as batteries.
- A typical example of electrochemistry in action is the _____ (see below). The diagram below shows chemicals being converted into electricity.



- The voltmeter is in place to show that electrons are flowing through the wire from the aluminium to the copper (more about this later).
- The reaction occurring is $3 \text{Cu}^{2+}(\text{aq}) + 2 \text{Al}(\text{s}) \rightarrow 3 \text{Cu}(\text{s}) + 2 \text{Al}^{3+}(\text{aq})$
- This reaction is moving electrons only!
- This reaction can be broken into two parts. _____ and _____
- Each half of the electrochemical cell is called a half-cell or half-reaction.

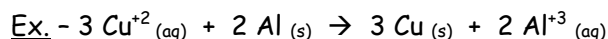
Definitions:

- 1.) An oxidation reaction is a half-reaction that _____ **electrons**.
Ex. - $2 \text{Al}(\text{s}) \rightarrow 6 \text{e}^- + 2 \text{Al}^{3+}(\text{aq})$
- 2.) A reduction reaction is a half-reaction that _____ **electrons**.
Ex. - $3 \text{Cu}^{2+}(\text{aq}) + 6 \text{e}^- \rightarrow 3 \text{Cu}(\text{s})$

Memory Aid #1

LEO ... Loss of electrons is oxidation
the lion says
GER ... Gain of electrons is Reduction

3.) A reaction that involves two half reactions is called a reduction-oxidation reaction or REDOX reaction.



4.) An oxidizing agent is _____ during a reaction.

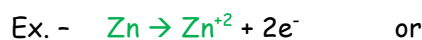
Ex. - In the above full reaction the Cu^{+2} is the chemical causing Al to be come oxidized (lose e^-), so the Cu^{+2} is called an **oxidizing agent**.

5.) A reducing agent is _____ during a reaction.

6.) Ex. - In the above full reaction the Al is the chemical causing Cu^{+2} to be come reduced (gain e^-), so the Al is called a **reducing agent**.

***** anytime an atom or ion changes its charge in a reaction, it is a REDOX reaction*****

- Oxidation reactions can be identified whenever a species become MORE POSITIVE (think number line).



- Reductions reactions can be identified whenever a species become MORE negative (think number line).



Oxidation Numbers

- Oxidation numbers are imaginary numbers that an atom WOULD POSSESS if the chemical containing the atom were made up of ions.

- _____ are USUALLY an oxidation # of +1 and the alkaline earth metals are always +2.

***Be careful of hydrogen when it is a Hydride. Ex. - LiH or NaH. Its charge is now -1.

- _____ are always an oxidation number of -1 and _____ is -2.

***Be careful of oxygen when it is a peroxide. Ex. - H_2O_2 , Ba_2O_2 , Na_2O_2 . Its charge is now -1.

- REMEMBER - _____.

Ex. - What is the oxidation number on the phosphorus of $\text{H}_4\text{P}_2\text{O}_7$?

$$\begin{array}{l} \text{H} = +1 \times 4 \quad \text{H} = +4 \quad \text{O} = -2 \times 7 \quad \text{O} = -14 \quad \text{P} = x \times 2 \quad \text{P} = 2x \\ 4 + 2x - 14 = 0 \quad x = +5 \quad \text{P} = +5 \end{array}$$

Ex. 2 - What is the oxidation number on the sulphur of S_8 ?

Predicting if a Reaction Occurs

- To predict if a reaction will proceed one needs to look at [The Table of Standard Reduction Potentials](#) chart.

This table is also known as the Standard Reduction Potential Table (E° Table).

- This table is used to . . .

- Predict which spontaneous reactions are likely to occur

- _____
- Calculate voltages produced by spontaneous reactions or voltages required to force non-spontaneous reactions.

- Things to note - 1. Generally, _____ are on the **bottom right**.
- 2. _____ (oxygen compounds) are in the **upper left**.
- 3. Some metals (ie. Fe, Sn, Cu, Cr, Hg) have **more than one** common oxidation number and appear on the chart as more than one half reaction.

*** This table functions a lot like the "acids chart" in that upper left chemicals tend to "go forward" (reduction) and the lower right tend to "go backwards" (oxidation), but all reactions can go either direction (oxidation or reduction).

Note - Half-reactions are drawn with equilibrium arrows as the reaction can go both directions. Ex. - $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-}$

When the half-reaction is part of a REDOX reaction then it is being forced to go one direction so write the arrow in the one direction of travel. Ex. - $\text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn}$

- The half-reaction that is higher on the left is the reaction that will undergo reduction (forwards reaction) and the lower reaction will be forced to undergo oxidation (backwards reaction).
- If both reactant chemicals appear on the same side of the chart **only**, _____!

Ex. - A reaction involving Cu and Zn metal. $\text{Zn}^{2+} + 2e^{-} \rightarrow \boxed{\text{Zn}}$ and $\text{Cu}^{2+} + 2e^{-} \rightarrow \boxed{\text{Cu}}$

- If the two reacting species are on opposite sides, it **may** or **may not** proceed. To proceed the reactant being reduced _____!

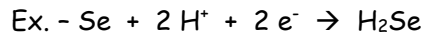
Ex. - A reaction involving Cu^{2+} and Zn metal. $\text{Zn}^{2+} + 2e^{-} \rightarrow \boxed{\text{Zn}}$ and $\boxed{\text{Cu}^{2+}} + 2e^{-} \rightarrow \text{Cu}$
 Cu^{2+} is higher and being reduced. **Spontaneous!**

Ex. - A reaction involving Zn^{2+} and Cu metal. $\boxed{\text{Zn}^{2+}} + 2e^{-} \rightarrow \text{Zn}$ and $\text{Cu}^{2+} + 2e^{-} \rightarrow \boxed{\text{Cu}}$
 Zn^{2+} is lower to be reduced. **No Reaction!**

- When looking at E° values, a positive E° value indicates that a net reaction is likely spontaneous, while a negative E° value indicates a net reaction is definitely non-spontaneous.
- For reduction reactions the E° value is used as written. For oxidation reactions the opposite E° value is used.

Ex. - **reduction** $\text{I}_{2(s)} + 2e^{-} \rightarrow 2\text{I}^{-}$ $E^{\circ} = 0.54\text{ V}$ **oxidation** $2\text{I}^{-} \rightarrow \text{I}_{2(s)} + 2e^{-}$ $E^{\circ} = -0.54\text{ V}$

- Some REDOX reactions will have H^+ in the reaction. The H^+ should be treated as a second reactant. The H^+ is showing this reaction is occurring in the presence of an acid, shown as H^+ or acidic. **Without the H^+ this reaction will NOT proceed and the H^+ should not be assumed to be present if not stated.**



- Rarely, a chemical species may undergo both reduction and oxidation. This is called disproportionation.

Balancing Half-Reactions

- Half reactions need to be balanced for both mass (atoms) and charge.
- the following steps will allow you to balance any redox equation:
 - 1.) Balance the **major**** atoms by inspection. **major atoms are all atoms that are not oxygen or hydrogen.
 - 2.) Balance **oxygen** atoms by adding H_2O molecules.
 - 3.) Balance the **hydrogen** atoms by adding H^+ .
 - 4.) Balance the overall **charge** by adding electrons.

MEMORY AID	"Major Hydroxide"	translated to " MAJOR OH⁻ "
1.) Balance MAJOR species.		(MAJOR)
2.) Balance the O atoms.		(O)
3.) Balance the H atoms.		(H)
4.) Balance the charge, using e^-		(-)

- Ex 1 - Balance the following half-reaction. $RuO_2 \leftrightarrow Ru$, which occurs in acid solution.

- Answer -
- 1.) Balance major atoms first.
 - 2.) Balance the O's by using H_2O 's.
 - 3.) Balance the H's by using H^+ 's.
 - 4.) Balance the charge by adding e^- .

- Ex 2 - Balance the following half-reaction. $Cr_2O_7^{2-} \leftrightarrow Cr^{+3}$, which occurs in acid solution.

- Answer -
- 1.) Balance major atoms first.
 - 2.) Balance the O's by using H_2O 's.

3.) Balance the H's by using H⁺'s.

4.) Balance the charge by adding e⁻.

- Ex 3. - Balance the following half-reaction. Pb ↔ HPbO₂⁻, which occurs in **basic** solution.

Answer - ***Balance as in **acid** first and then we will convert it to basic after.***

1.) Balance major atoms first.

2.) Balance the O's by using H₂O's.

3.) Balance the H's by using H⁺'s.

4.) Balance the charge by adding e⁻.

5.) Convert to basic by adding the **water equilibrium** to cancel all the H⁺. H₂O ↔ H⁺ + OH⁻



Balancing REDOX Using Half-Reactions

- There are two methods for balancing REDOX reactions; half-reactions and oxidation numbers. You need to know one way. I recommend both ways as I use both. Each way is better under certain conditions. *Oxidation* is quicker for *simple equations* and *half-reactions* are simpler for more *complex questions*. Knowing both will make chemistry quicker and easier.

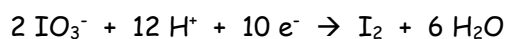
1.) Half-reaction Method



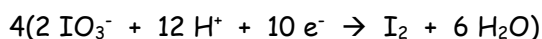
Step 1 - Break into half-reactions



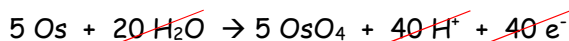
Step 2 - Balance each half-reaction

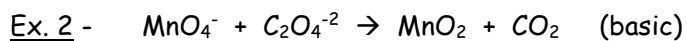


Step 3 - Balance electrons by multiplying reactions by whole numbers



Step 4 - Add the two half-reactions, and cancel common species.





Step 1 - Break into half-reactions

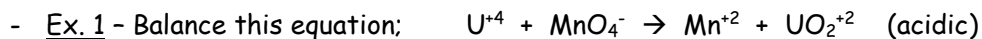
Step 2 - Balance each half-reaction

Step 3 - Balance electrons by multiplying reactions by whole numbers

Step 4 - Add the two half-reactions, and cancel common species.

Balancing REDOX Using Oxidation Numbers

- In balancing REDOX using oxidation numbers always remember that the overall change in oxidation numbers must be zero!



Step 1 - Balance major atoms and assign oxidation numbers to all chemicals that have a change in oxidation number (ΔON).

Step 2 - Since the total $\Delta ON = 0$, multiply each half reaction by the oxidation numbers involved.

Step 3 - Add the reactions back together.

Step 4 - Finish reaction by balancing the O's and H's as done in half reaction balancing.

Ex. 2 - Balance $\text{Zn} + \text{As}_2\text{O}_3 \rightarrow \text{AsH}_3 + \text{Zn}^{+2}$ (basic)

Step 1 - Balance major atoms and assign oxidation numbers to all chemicals that have a change in oxidation number (ΔON).

Step 2 - Since the total $\Delta ON = 0$, cross multiply each half reaction by the oxidation numbers involved.

Step 3 - Add the reactions back together.

Step 4 - Balance the O's and H's as done in half reaction balancing.

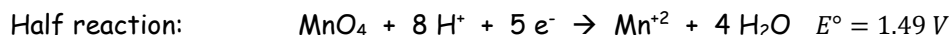
Step 5 - Finish reaction (in basic) by adding water equilibrium as done in half reaction balancing.

Redox Titrations

- Acid-base reactions are often a REDOX reaction. As such, an understanding of oxidation and reduction reactions can be very beneficial to titration reactions.

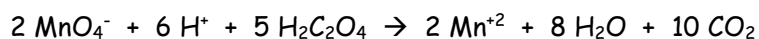
Oxidizing and reducing agents

- A common **reducing agent** is I^- . This ion is usually added by using common salts like NaI or KI.
- The most popular **oxidizing agent** is probably KMnO_4 (the K is a spectator ion).



- MnO_4 is often popular due to it having a VERY strong tendency to be reduced and because KMnO_4 is a dark **magenta** and Mn^{+2} is **colourless**. As the MnO_4 is added the solution starts to turn magenta but then the MnO_4 reacts and the magenta disappears. When the redox reaction is completed the next drop of MnO_4 to the solution will cause a light magenta colour which WON'T disappear.

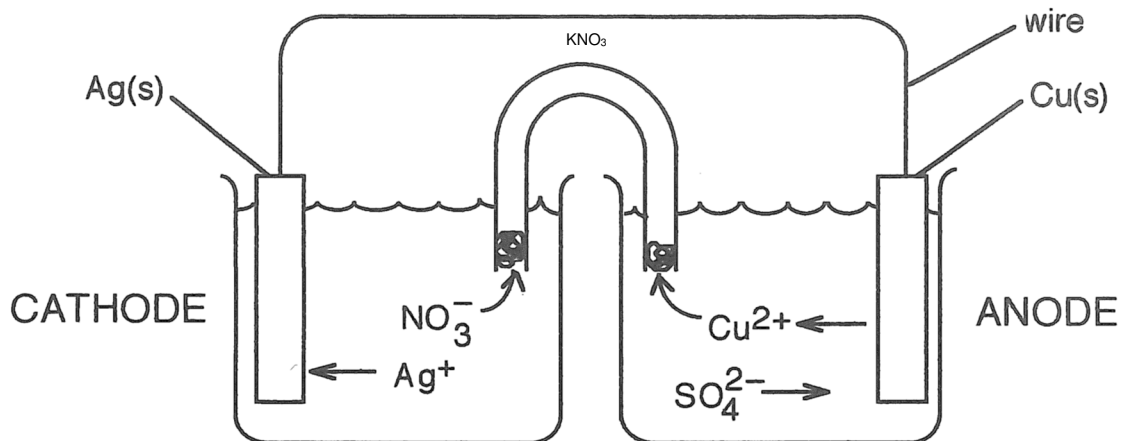
Ex. - When 25.00 mL of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is titrated to the endpoint with acidic KMnO_4 , the titration requires 15.4 mL of 0.100 M KMnO_4 . What is the concentration of oxalic acid in the solution?



Answer -

Electrochemical Cells

- We're going to revisit electrochemical cells and look at the details of how the REDOX reaction produces current (electricity).



- The two half-reactions are $\text{Ag}_{(s)} \rightarrow \text{Ag}^+ + e^-$ and $\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+} + 2e^-$
- Ag is higher on the chart and therefore will undergo reduction while Cu will oxidize. The Cu will build up electrons on its surface. These electrons will travel through the wire to the Ag. Thus, the Cu loses electrons (oxidized) and becomes the _____.
- The electrons in the wire go into the Ag electrode, this upsets the equilibrium (Le Chatelier's Principle) forcing Ag⁺ to reduce. Therefore, reduction occurs at the Ag electrode and it is the **cathode**.

Memory aid

AN OX CARED

Anode is **O**xidation

Cathode is **R**eduction

- The salt bridge (KNO₃ as an example) allows the movement of the ions into or out to keep the charges balanced in each cell.
- Ex. - Ag⁺ is forming Ag_(s) so the Ag⁺ needs to be replaced by the K⁺ ion to maintain neutrality in the half-cell.
- The cell is "dead" when a solution of ions is consumed, an electrode is dissolved, or the salt bridge diffuses away.

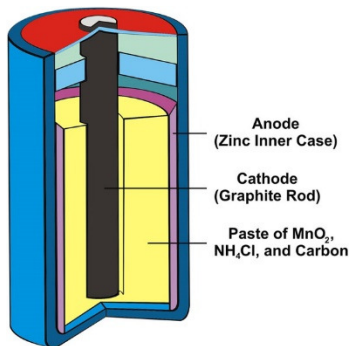
Applied Electrochemical Cells

1.) Batteries

- _____
 - Commonly these are lead-acid storage batteries.
 - Cathode is Pb coated in PbO₂, anode is pure Pb, and the electrolyte is H₂SO₄.
 - Anode (oxidation) = $\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$ $E^\circ = 0.35 \text{ V}$
 - Cathode (reduction) = $\text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ $E^\circ = 1.60 \text{ V}$

Overall

- Over time both plates become coated in PbSO₄ stopping the spontaneous reaction.
- H₂SO₄ is consumed in the reaction, so measuring the [H₂SO₄] or the density of the electrolyte allows charged state of battery to be measured.
- "Recharging" occurs by reversing e⁻ flow to drive the reaction in reverse (charging system in car).
- _____
 - Alkaline or carbon-zinc "batteries". These differ in the electrolyte being a paste instead of a liquid (hence dry cell).



Zinc-Carbon battery

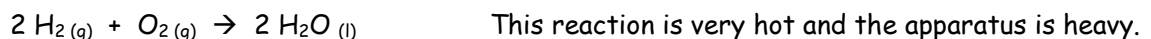
- As the zinc is used up (oxidized), Zn(NH₃)₄⁺² accumulates around the anode and the battery wears out.

Alkaline

- Same design as zinc-carbon but the electrolyte (KOH) is "alkaline" (basic).

2.) Fuel Cells

- Galvanic cell (electrochemical cell) in which reactants are continuously supplied to make electricity.
- The most common is the hydrogen-oxygen fuel cell as hydrogen and oxygen are cheap (free) and plentiful.
- The reaction is used by NASA and private companies (hello SpaceX) to power rockets.

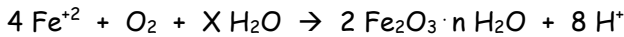


3.) Corrosion

- When iron (steel) is smelted there are very small amounts of impurities and stress points. These impurities and stress points set up anodic and cathodic regions in the metal.
- The anodic region results in Fe dissolving $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$

The e^- flow through the metal to the cathodic region where O_2 reacts $O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$

The Fe^{+2} diffuses through the water droplet to the surface to react with the O_2 .



- To prevent corrosion . . .
 1. Paint it or cover in a thin layer of plastic. Why?
 2. Apply a thin layer of corrosion resistant metal (more on this next section).
Ex. galvanized steel. Zinc is plated on the steel. Zinc gets scratched and forms zinc oxide.
 3. Apply a metal that forms a strong oxide layer (anodizing).
 4. Cathodic protection (see below).
 5. Remove chemicals like oxygen that cause corrosion.

Cathodic Protection

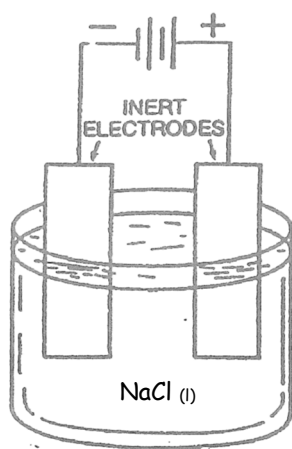
- The process of allowing a non-critical metal be sacrificially oxidized in place of an important metal to protect it.
- Common in _____ to protect ship hulls or outboard motors. Aluminium engines are in contact with numerous ions from dissolved salts. Many of the cations of these salts are above and to the left of aluminum on the E° table, resulting in the salt metal ions reducing and the aluminium engine oxidizing!
- The answer to stop this is to attach a metal that is lower on the RHS (_____) to sacrificially oxidize in place of my expensive engine. The Mg must be directly attached to the aluminium and below the water line.

Electrolytic Cell or Electrolysis

- This type of cell is constructed by _____ a current through a cell with a negative cell potential (E°). This current will force a non-spontaneous reaction to occur.

- The absolute value of the negative cell potential is the minimum voltage needed to drive this reaction.
- The reduced species will be the highest on the left of the table and the oxidized species will be lowest on the right.
- In an _____ (spontaneous cell) the combination of chemicals producing the greatest voltage will react, while in the _____ (non-spontaneous), the combination of chemicals requiring the least voltage will react.
- The negative side of the battery that drives the reaction leads to the cathode and the positive side leads to the anode.

A Type I Electrolytic Cell



Note - **inert electrodes** must be made of conducting material which is not inclined to undergo a REDOX reaction or melt. Typically carbon and platinum are used but sometimes gold can be used in a pinch (high on table).

Ex. - Write the reduction half-reaction

$E^\circ =$

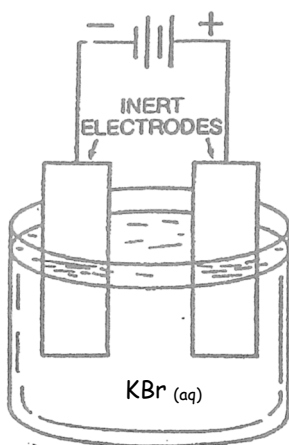
Write the oxidation half-reaction

$E^\circ =$

Write the net reaction

$E^\circ =$

A Type II Electrolytic Cell



***Note - this situation has the salt in water which adds a complication.

It's now possible that water may become the easiest species to oxidize or reduce and may therefore be involved in the reaction in place of the salt. The reactions that produce the **lowest overall voltage** will occur. (Check water it appears TWICE)***

*****Always consider water as a reactant in a type II problem.*****

Ex. - The species present are K^+ , Br^- , and H_2O

Write the reduction half-reaction

$E^\circ =$

Write the oxidation half-reaction

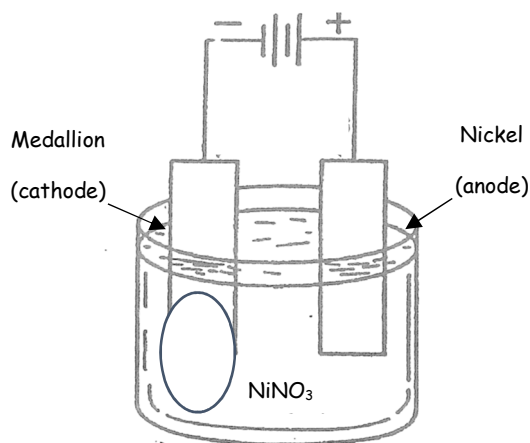
$E^\circ =$

Write the net reaction

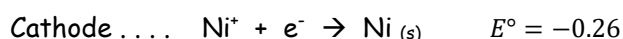
$E^\circ =$

- In the above reaction water should have been oxidized preferentially to Br^- . This didn't occur as oxidizing H_2O to O_2 (very kinetically slow process) takes more voltage than oxidizing Br^- to Br_2 . This phenomenon is known as the _____.
- In other words, the **overpotential effect** is showing how reality is different with water compared to theory. In practice then the water is ACTUALLY found where the arrow tip is on the chart!
- You don't need to know the overpotential effect, just memorize that solutions containing Cl^- , and Br^- both oxidize to Cl_2 and Br_2 at the anode before water.

A Type III Electrolytic Cell



***Note - the medallion will have the nickel plate onto it as it is the cathode. The anode needs to be nickel metal to constantly oxidize and replenish the Ni^{+2} ions as they reduce onto the medallion. The solution needs to be the ion being reduced onto the medallion (Ni^+) with a soluble anion (NO_3^-) so it doesn't precipitate out.



- These cells are used to either electroplate metals (above) or in purify metals in an industrial process in a smelter.
- In both cases the solution and anode must be made of the same type of metal. The cathode must conduct electricity and be _____ water on the RHS (right hand side) of the E° table.
- To purify metals the impure metal solid (anode) will dissolve in to the solution and ultimately plate onto the cathode. The impurities in the anode will fall to the bottom and form a sludge.