Electrochemistry

Definition: the study of all reactions in which the transfer of electrons take place.

These reactions may:

1. Produce electricity (batteries)
2. Require electrical energy to take place (charging batteries)
3. Occur in the absence of electricity (formation of any ionic compound)

<u>Historical Perspective</u>

Example: rusting of iron, combustion reactions (example of **<u>oxidation</u>**). The opposite of oxidation is **<u>reduction</u>** (Formation of metal from its compounds) Example : iron ore is reduced to pure iron

<u>Modern Perspective</u>

Oxidation - the loss of electrons
Reduction - the gain of electrons

In a chemical reaction whereby one species loses electrons there must be a chemical species that gains electrons. These occur simultaneously. This type of reaction is called REDOX (**<u>red</u>**uction - **<u>ox</u>**idation)

Example : a piece of zinc is added to a solution of copper (II) sulfate. $CuSO_4$ dissociates in solution, therefore

$$Zn\ (s) + CuSO_4\ (aq) \rightarrow Cu\ (s) + ZnSO_4\ (aq)$$

$$Zn\ (s) + Cu^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightarrow Cu\ (s) + Zn^{2+}\ (aq) + SO_4^{2-}\ (aq) \qquad \textbf{Total Ionic Equation}$$

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Cu\ (s) + Zn^{2+}\ (aq) \qquad \textbf{Net Ionic Equation}$$

<u>Redox reactions will always be balanced - any electrons lost by one species are gained by the other species ∴ there will be no overall change in charge - reactants versus products.</u>

Finally to remember which species is oxidized and which species is reduced, use the following mnemonic :

OIL RIG - **O**xidation **I**nvolves **L**oss **R**eduction **I**nvolves **G**ain

or LEO GER - **L**ose **E**lectrons **O**xidize **G**ain **E**lectrons **R**educe

(They may be sad, but they are effective as a way to remember!)

Half Reactions

- Each redox reaction can be separated into two halves; one for oxidation and one for reduction. When the "half reactions" are written, the number of electrons is included on either the reactant or product side as necessary.
- For example, the half reactions for the previous system would be:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$ ox (lost 2e-)
$Cu^{2+}(aq) + 2e- \rightarrow Cu(s)$ red (gain 2e-)

- To identify and write the half reactions in a redox equation you must:
  1. Identify the species being oxidized and reduced
  2. Write the appropriate products
  3. Place the correct number of electrons on the appropriate side of the arrow.

- Ex: Write the balanced half reactions from the following net ionic equations.

1) $Al(s) + Fe^{3+}(aq) \rightarrow Al^{3+}(aq) + Fe(s)$
$Al(s) \rightarrow Al^{3+} + 3e-$ ox (lost 3 e^-)
$Fe^{3+}(aq) + 3e- \rightarrow Fe(s)$ red (gained 3 e^-)

2) $2Ag^+ (aq) + Cu (s) \rightarrow 2Ag (s) + Cu^{2+} (aq)$
$Cu (s) \rightarrow Cu^{2+} (aq) + 2e^-$ ox
$2Ag^+ (aq) + 2e^- \rightarrow 2 Ag (s)$ red

- You must also write balanced half reactions from the redox reaction. First determine the Net Ionic Equation then follow the previous steps.

- Ex: Write the balanced half reactions from the following redox reactions:

1) $Sn(s) + PbCl_2 \rightarrow SnCl_2(aq) + Pb(s)$
$Sn(s) + Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow Sn^{2+}(aq) + 2Cl^-(aq) + Pb(s)$ TIE
$Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+} + Pb(s)$ NIE
$Sn(s) \rightarrow Sn^{2+}(aq) + 2e-$ ox
$Pb^{2+}(aq) + 2e- \rightarrow Pb(s)$ red

2) $3Zn(s) + Fe_2(SO_4)_3(aq) \rightarrow 3ZnSO_4(aq) + Fe(s)$
$3Zn(s) + 2Fe^{3+}(aq) + 3SO_4^{2-}(aq) \rightarrow 3Zn^{2+}(aq) + 3SO_4^{2-}(aq) + 2Fe(s)$
$3Zn(s) + 2Fe^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Fe(s)$
$3Zn(s) \rightarrow 3Zn^{2+}(aq) + 2e-$ ox
$2Fe^{3+}(aq) + 3e- \rightarrow 2fE(s)$ red

Summing Half Reactions

- Given 2 half reactions, they can be added like Hess' law to determine the overall reaction...the electrons should cancel or you have done something wrong.

Ex: $Zn \rightarrow Zn^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

More Definitions: **Reducing Agent - the species that loses electrons so that other species be reduced**

Oxidizing Agent - the species that gains electrons from the reducing agent

Identification of redox species

- Given a redox reaction you must be able to identify the following species:
  1.Oxidized
  2.Reduced
  3.Oxidizing Agent (OA) ((Not ion...go back to original equation))
  4.Reducing Agent (RA)
- To determine this, examine the **reactants only**!

Ex: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
R O
OA RA

- The species being oxidized is the reducing agent.
- The species being reduced is the oxidizing agent.

Oxidation Numbers

- To determine whether the reaction is redox we must identify chemical species that are being oxidized or reduced. This is not always easy since reactions do not usually show electrons. Each chemical species is assigned an oxidation number. The species are then compared (reactant vs. product)...if the oxidation number changes then the species lost or gained electrons and therefore it would be a redox reaction.

- **Definition of Oxidation Number -** actual or hypothetical charges assigned to a chemical species

RULES (**THESE MUST BE MEMORIZED**)

1. Pure elements have an oxidation number of zero (oxidation number of Fe (s) is 0)

2. Oxidation number of a monotomic ion is the same as its charge(the Al in Al^{3+} has an oxidation number of +3)

3. The oxidation number of hydrogen in its compounds is always +1 except in metal hydrides, where it is -1 (the oxidation number of H in CH_4 is +1, but in CaH_2, it is -1)

4. Oxidation number of oxygen is usually 2- (except in H_2O_2 it is -1, and OF_2 is +2)

5. In a covalent compound that does not contain "O" or "H", the more electronegative element is assigned an oxidation number equal to its negative charge (Cl in PCl_5 is -1)

6. ****** In a compound all oxidation numbers must add up to 0

7. The sum of all oxidation numbers in a polyatomic ion equals the charge on the ion (In SO_4^{2-} , there are 4 O which is 4 x -2 = -8, total charge is -2, so the oxidation number on the S must be -2 - -8 which equal +6, therefore the oxidation number of the S is +6

Let's apply the rules (oh yes, let's!)

Mg (s)	Oxidation number is 0	(Rule #1 - elements are 0)
Br_2 (l)	Oxidation number is 0	(Rule #1 - elements are 0)
$MnCl_2$	Oxidation number for Cl is -1 (Rule # 2, monatomic ion) Oxidation number for Mn is +2 (Rule #6 - must add up to 0, there are two Cl, each is -1, so that's -2, therefore Mn must be +2)	
VO_3	Oxidation number for oxygen is -2 Oxidation number for V must be +6	(Rule #4 - oxygen is -2) (Rule #6 - must total 0, and there are 3 O @ -2 each)
CO_2	Oxidation number of O is -2 Oxidation number for C must be +4	

MnO_4^- Oxidation number of O is -2
Total of a polyatomic ion must be its charge, there are 4 oxygen so that's -8, and -1 - -8 = +7,so:
Oxidation number of Mn is +7

PO_4^{3-} Total must be 3-, there are 4 oxygen, so that's -8, that means the P must be +5
Oxidation number of O is 2-
Oxidation number of P is +5

Application of Oxidation Numbers to Redox Reactions

To determine the redox half-reactions for a chemical reaction, you must first determine whether the reaction is redox or not. To do this, assign oxidation numbers to each atom or ion and then compare.....if the oxidation numbers do not change it is not a redox reaction. If the ox numbers change, then determine which species was oxidized/reduced and write the "half-reaction" for it.

Example: $PbCl_4(aq) + 2\ Zn(s) \rightarrow 2\ ZnCl_2(aq) + Pb(s)$

ox# +4 -1 0 +2 -1 0

ox # of Pb^{4+} has changed from +4 to 0.......it was **reduced**/ $PbCl_4$ is the oxidizing agent
ox # of Zn has changed from 0 to +2......it was **oxidized**/ Zn is the reducing agent

therefore, this is a redox reaction.....now write the half-reactions

$Pb^{4-}(aq) + 4e^- \rightarrow Pb(s)$

$2\ Zn(s) \rightarrow 2\ Zn^{2+}(aq) + 4e^-$

There are some helpful hints to determine redox reactions:

1. **Any reaction involving an element as a reactant or product is redox**
2. **Any double replacement reaction is never redox**

New Way to Define Oxidation and Reduction:
oxidation - an increase in oxidation number
reduction - a decrease in oxidation number
Examples:

identify changes in oxidation number in the following reactions:

a) $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(aq)$

ox # +1 -1 +1 +5 -2 +1+5-2 +1 -1
since there is no change in ox # this reaction is not redox

b) $CH_4(g)$ + 2 $O_2(g)$ ➜ $CO_2(g)$ + $H_2O(g)$

ox # -4 +1 0 +4-2 +1 -2

C has changed ox # from -4 to +4........is oxidized/ CH_4 is the reducing agent
O has changed ox # from 0 to -2..........is reduced/ O_2 is the oxidizing agent

Writing and Balancing Half Reactions

When simple composition or decomposition reactions for ionic compounds are involved, their half reactions can be used to determine the original net-ionic equation. To do this, you must add up each half reaction. However, the total number of electrons must balance on both sides (for them to cancel) so it is possible one or both reaction must by multiplied by the appropriate integer.

Ex: given the following half reactions, determine the overall reaction:

1. $Au^{3+} + 3e^- \rightarrow Au$
2. $Zn \rightarrow Zn^{2+} + 2e^-$

Ans the number of electrons do not balance, use the least common multiple to balance....multiply equation 1 by 2 and equation 2 by 3

$2\ Au^{3+} + 6e^- \rightarrow 2\ Au$
$3\ Zn \rightarrow 3\ Zn^{2+} + 6e^-$

add the reactions to give $2\ Au^{3+} + 3\ Zn \rightarrow 2\ Au + 3\ Zn^{2+}$

double check......conservation of matter (including charge) must occur

Most reactions are not as simple as composition/decomposition. It is possible to have more complicated reactions. The half reactions for these reactions are usually obtained from a standard reduction potential table for simple redox reactions (data tables)

Rules for Identifying Redox Reactions:

1. **Double replacement reactions are NEVER Redox**
2. **ALL combustion, single replacement, formation and decomposition ARE**
3. **OA and RA are always reactants <u>never</u> products**

<u>Writing Balanced equations for complex redox reactions occurring in acidic or basic solutions</u> (long answer question)

Many redox reactions occur only in acidic or basic solutions.....the extra hydrogen ions (H^+) or hydroxide ions (OH^-) enable the redox to occur more readily. These ions, as well as water, are used to balance the number of oxygen atoms and hydrogen atoms.

This process involves many steps....**they must be memorized**:

To balance redox equations under acidic conditions:

1. Separate the 2 half reactions...leave unbalanced (oxd and red)
2. Balance all atoms except O and H
3. Balance O atoms using water molecules
4. Balance H atoms using H^+
5. Balance charges with e^-
6. Balance number of e^- for both reactions (to cancel after)
7. Add the half reactions

Balance the following ionic equation under acidic conditions:

$ClO_4^-(aq) + NO_2(g) \rightarrow Cl^-(aq) + NO_3^-(aq)$

1.ox# +7 -2 +4 -2 -1 +5 -2 separate out the half reactions

$NO_2(g) \rightarrow NO_3^-(aq)$ (ox)
$ClO_4^-(aq) \rightarrow Cl^-(aq)$ (red)

2. Balance N atoms.....already balanced....................balance Cl atoms...already balanced
$NO_2(g) \rightarrow NO_3^-(aq)$ $ClO_4^-(aq) \rightarrow Cl^-(aq)$

3. Balance O atoms
$H_2O + NO_2(g) \rightarrow NO_3^-(aq)$ $ClO_4^-(aq) \rightarrow Cl^-(aq) + 4\ H_2O$

4. Balance H atoms

H_2O + NO_2(g) ➜ NO_3^-(aq) + 2 H^+ 8 H^+ + ClO_4^-(aq) ➜ Cl^-(aq) + 4 H_2O

5. Balance charges with e^-

H_2O + NO_2(g) ➜ NO_3^-(aq) + 2 H^+ + 1e^- 8 H^+ + ClO_4^-(aq) +8e^- ➜ Cl^-(aq) + 4 H_2O

6. Balance e^- (multiply by 8)

8 H_2O + 8NO_2(g) ➜ 8NO_3^-(aq) + 16 H^+ + 8e^- 8 H^+ + ClO_4^-(aq) + 8e^- ➜ Cl^-(aq) + 4 H_2O

7. Add them up!

8 H_2O + 8NO_2(g) ➜ 8NO_3^-(aq) + 16 H^+ + 8e^-
8e^- + 8 H^+ + ClO_4^-(aq) ➜ Cl^-(aq) + 4 H_2O

8NO_2(g) + ClO_4^-(aq) + 4 H_2O ➜ Cl^-(aq) + 8NO_3^-(aq) + 8 H^+

To balance redox equations under basic conditions:

Follow the same steps as under acidic conditions, but, there is an extra step.....balance out the H^+ ions by adding OH^- ... this will leave OH^- in your overall redox reaction, which is expected since it is in basic conditions:

1. Separate the 2 half reactions...leave unbalanced (oxd and red)
2. Balance all atoms except O and H
3. Balance O atoms using water molecules
4. Balance H atoms using H^+
5. Balance H^+ using OH^-, but add to **BOTH** sides of equation
6. Combine any H^+ and OH^- to make water on one side of the equation (and cancel any that can be cancelled)
7. Balance charges with e^-
8. Balance number of e^- for both reactions (to cancel after)
9. Add the half reactions

Example:

Balance the following ionic equation under basic conditions:

CN^-(aq) + MnO_4^-(aq) ➜ CNO^-(aq) + MnO_2(aq)

1.ox# +2-3 +7 -2 +4-3-2 +4 -2

CN^-(aq) ➜ CNO^-(aq) (ox)
MnO_4^-(aq) ➜ MnO_2(aq) (red)

2. CN^-(aq) ➜ CNO^-(aq) MnO_4^-(aq) ➜ MnO_2(aq)

already balanced

3. Balance O atoms using water

H_2O + CN^- ➜ CNO^- MnO_4^- ➜ MnO_2 + 2H_2O

4. Balance H atoms using H^+

H_2O + CN^- ➜ CNO^- + 2H^+ 4H^+ + MnO_4^- ➜ MnO_2 + 2H_2O

5. Add OH^- to BOTH SIDES to balance H^+

$2OH^- + H_2O + CN^- \rightarrow CNO^- + 2H^+ + 2OH$

$4OH^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O + 4OH^-$

6. Combine H^+ and OH^-

$2OH^- + H_2O + CN^- \rightarrow CNO^- + 2H_2O$

$2OH^- + CN^- \rightarrow CNO^- + H_2O$

$4H_2O + MnO_4^- \rightarrow MnO_2 + 2H_2O + 4OH^-$ becomes

$2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$

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7. Balance charges with e^-

$2OH^- + CN^- \rightarrow CNO^- + H_2O + 2e^-$

$3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$

8. Balance e^- (multiply by 2 and 3 to reach LCM of 6)

$6OH^- + 3CN^- \rightarrow 3CNO^- + 3H_2O + 6e^-$

$6e^- + 4H_2O + 2MnO_4^- \rightarrow 2MnO_2 + 8OH^-$

9. Add up the half reactions

$6OH^- + 3CN^- \rightarrow 3CNO^- + 3H_2O + 6e^-$

$6e^- + 4H_2O + 2MnO_4^- \rightarrow 2MnO_2 + 8OH^-$

$H_2O + 2MnO_4^- + 3CN^- \rightarrow 3CNO^- + 2MnO_2 + 2OH^-$

Try these two:

Balance the reaction below under acidic conditions.

$$N_2H_4 + MnO_4^- \rightarrow N_2 + Mn^{2+}$$

Balance the redox reaction below under basic conditions.

$$Cr_2O_7^{2-}(aq) + I^-(aq) \rightarrow I_2(s) + Cr^{3+}(aq)$$

Redox Stoichiometry

- As in previous stoichiometry items (such as xlr in a/b) the concept of stoich can be applied to redox reactions. There is no difference in the procedure, it is still a three-step procedure.
- Redox stoichiometry problems are spontaneous reactions that proceed to form products as when reactants are mixed. The reaction does not require energy or a catalyst to proceed.
- This could be a redox titration or a simple redox reaction.
- For example:

An analyst titrates an acidified solution containing 0.153 g of sodium oxalate, $Na_2C_2O_4$, with a potassium permanganate solution, $KMnO_4$. The purple endpoint is reached when 41.45 mL of $KMnO_4$. What is the molar concentration of the $KMnO_4$ solution, given the balanced equation for this titration is:

$$2\ MnO_4^{-}(aq) + 5\ C_2O_4^{2-}(aq) + 6\ H^{+} \rightleftharpoons 2\ Mn^{2+}(aq) + 10\ CO_2(aq) + 8\ H_2O(l)$$

Answer:
1. Set up your givens
2. Calculate the mol of $Na_2C_2O_4$ (not $C_2O_4^{2-}$)
3. Use the mole ratio formula (w/g is 2/5)
4. Calculate molar concentration of $KMnO_4$ using molar concentration formula

- This problem was a mass to molar concentration type. It could have been same problem but set up with a table of buret readings.
- For example:

25.00 mL of a solution containing iron(II) ions was titrated with 0.02043 mol/L potassium dichromate solution. Calculate the molar concentration of the iron(II) ions in the original acidic solution given the table of buret readings below and the balanced chemical reaction:

	Trial 1	Trial 2	Trial 3
final buret reading (mL)	42.56	39.56	48.59
initial buret reading (mL)	7.56	4.58	13.09

$$4\ Cr_2O_7^{2-}(aq) + 3\ Fe^{2+}(aq) + 8\ H^{+} \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq) + 4\ H_2O$$

Electrochemical Cells

Definition Electrochemical Cell

A device for interconverting chemical and electrical energy.

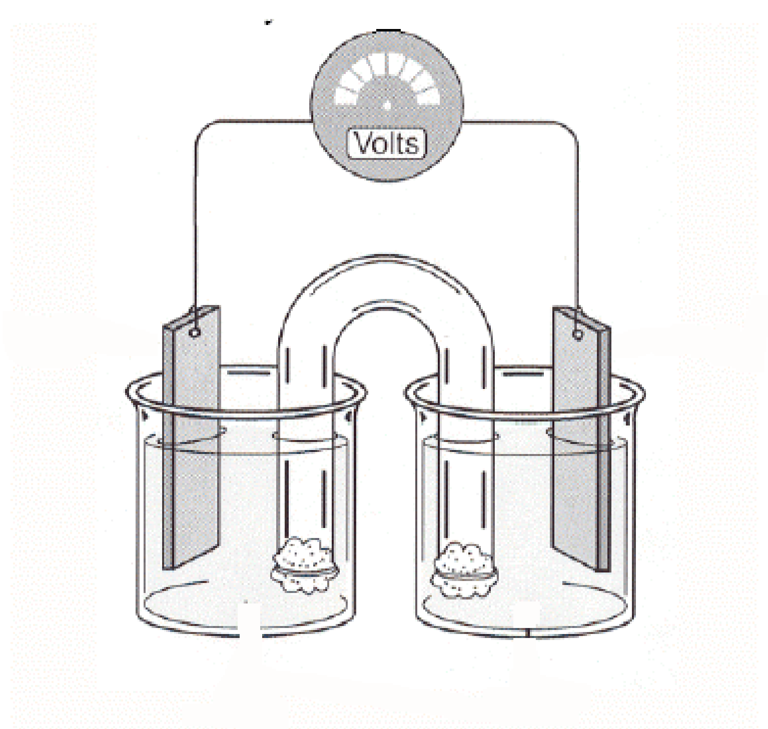
Example: A battery....takes energy released by a spontaneous chemical reaction and uses it to produce electricity.

- Is of tremendous importance to society because of industrial applications. Not only batteries but the production of many chemicals, such as NaOH, PVC, or the separation of copper metal or aluminum from ore.

- There are two other descriptors that are used interchangeably with electrochemical cell; **galvanic cell** or **voltaic cell**. For our purposes, these cells are considered to be equivalent galvanic cell/voltaic cell use a spontaneous reaction to generate a current)

- You must be able to draw and label an electrochemical cell, which includes the following parts:
    1. anode - electrode at which oxidation occurs
    2. cathode - electrode at which reduction occurs
    3. salt bridge - a connection between the anode and cathode that contains an inert electrolytic solution (does not interfere in the reaction).....it allows ions to migrate.....the ends of the salt bridge contain a porous plug.....does not let the electrolyte leak out quickly
    4. direction of electron flow......from anode to cathode
    5. Direction of flow of ions....anion to anode, cations to cathode

label this



How does an electrochemical cell work?

- Two electrodes, which carry electrons into and out of a cell are placed in electrolytes (electrolytic solutions that conduct electricity when dissolved in water)
- The electrodes are connected via an external circuit (such as a wire)
- A barrier separates the electrodes in their electrolytic solutions
- When the electrolytic solutions are connected by a salt bridge, it allows electrons from the anode to move to the cathode through the wire.
- The anode undergoes oxidation and produces electrons
- Conversely, the cathode undergoes reduction, gains electrons
- Ions in the electrolyte migrate towards the anode (and away from the cathode) to neutralize the change in charge of the solutions
- The salt bridge completes the electrical circuit. Without it, the solution in the anode compartment would become positively charged as cations are produced in it (oxidation) while the solution in the cathode department would become positively charged as cations are removed from it (reduction)

- To illustrate, examine the electrochemical cell with the two electrodes Sn and Tl.
- The thalium electrode is placed in thalium sulfate, tin is placed in tin sulfate
- The two electrodes are connected with a wire (which could be hooked up to a light bulb, a motor, or a voltmeter {which shows a change in voltage/electron movement}
- since Tl^{1+}ions are above Sn in the table of redox half-reactions, the oxidizing agent is Tl^{1+} and the reducing agent is Sn. Therefore, the tin electrode will be oxidized, Tl^{1+}will be reduced. The half-reactions will be:

$$Tl^{1+} + e^- \rightarrow Tl \quad (r)$$
$$Sn \rightarrow Sn^{2+} + 2e^- \ (o)$$

- Since tin is losing electrons, the flow of electrons will be from the tin electrode to the thalium electrode
- the tin electrode is called the anode (since it is producing electrons)
- the thalium electrode is called the cathode (since it is gaining electrons)
- electrons always flow from the anode to the cathode
- a salt bridge is added to connect the two electrolytic solutions
- sulfate ions migrate towards the anode to balance the production of tin cations
- cations (Sn^{2+}) ions migrate towards the cathode to replace the loss of the thalium ions Tl^{1+}
- This can be seen when the electrochemical cell is drawn below

Electrochemical Cell Notation

Electrochemical cells are very time consuming to draw and/or explain. An easier way to represent these cells is to use a shorthand method called electrochemical cell notation.

To write this notation:

1. a double vertical line is used to represent the salt bridge

   ‖

2. a single vertical line represents the electrode from their ion forms in solution

   |

3. by convention, the anode reaction appears on the left, the cathode reaction on the right

For example:

anode | anodic ion ‖ cathodic ion | cathode

for the previous example:

$Sn(s) \mid Sn^{2+}(aq) \parallel Tl^{1+}(aq) \mid Tl(s)$

- the reverse question is also testable, draw and label and electrochemical cell using electrochemical cell notation.

- Example:
  Given the following electrochemical cell notation, draw and label the electrochemical cell that it represents

anode is Cd, cathode is Pt and the half reactions are:

Oxidation half-reaction: $Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2e^-$

Reduction half-reaction: $H^+_{(aq)} + e^- \rightarrow H_{2(g)}$ (unbalanced)

$2H^+_{(aq)} + e^- \rightarrow H_{2(g)}$

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ (balanced)

To write the overall cell reaction, add the half-reactions.

$$Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2e^-$$

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

$$Cd_{(s)} + 2H^+_{(aq)} + 2e^- \rightarrow Cd^{2+}_{(aq)} + 2e^- + H_{2(g)}$$

Simplify by removing two electrons from both sides.

$Cd_{(s)} + 2H^+_{(aq)} \rightarrow Cd^{2+}_{(aq)} + H_{2(g)}$ (balanced)

Production of Energy in Electrochemical Cells

- Electrochemical cells are cells which produce electrical energy in spontaneous redox reactions. The production of electricity results from the flow of electrons from one half-cell to the other. These electrons move from the half-cell with higher potential energy to lower potential energy.
- Energy produced by a half-cell is called the half-cell voltage or half-cell potential....E^o
- The half-cell voltage is determined by connecting it to the Standard Half-Cell (Hydrogen Half-Cell......... $2H^+ + 2e^- \rightarrow H_2$)
- By convention, the standard half-cell voltage is 0.00 V
- Voltage is measured using a voltmeter
- The voltage of the half-cell is then the voltage shown on the voltmeter. (Since the difference between the voltage shown and zero is the voltage shown)
- For example:

  $Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^o = 0.34$ V

  $Zn^{2+} + 2e^- \rightarrow Zn$ $\quad E^o = 0.76$ V
- A list of half-cells are usually written from most positive to negative voltage (data table) called a Table of Standard Half Cell Potentials
- A spontaneous redox reaction has a positive (+ve) cell voltage....one that requires energy input has a negative cell voltage

Calculation of Cell Voltage

- Given an electrochemical cell, the half reactions can be used to calculate the voltage of the cell.
- Determine the half cell reactions, obtain their half-cell voltages from the TSHCP, and add them together

- Example: Determine the cell voltage for the following reaction:

  $Cu(s) + Fe^{2+}(aq) \rightarrow Cu^{2+}(aq) + Fe(s)$

  Answer: Write the half-cell reactions

  $Cu \rightarrow Cu + 2e^-$

  $Fe^{2+} + 2e^- \rightarrow Fe$

  Obtain their half-cell voltages from the TSHCP.....the half reaction for copper is the opposite as is in the table so the potential must be flipped

  $Cu \rightarrow Cu + 2e^-$ $\quad E^o = -0.34$ V

  $Fe^{2+} + 2e^- \rightarrow Fe$ $\quad E^o = -0.45$ V

  Add the half-cell voltages to obtain the cell voltage

  $Cu(s) + Fe^{2+}(aq) \rightarrow Cu^{2+}(aq) + Fe(s)$ $\quad E^o = -0.79$ V

Note: This reaction is not spontaneous.....in other words, copper will not react with the iron(II) ions (the opposite reaction would be spontaneous, that is, iron will reaction with copper(II) ions

Special Note: If the half reactions are not balanced, it does not matter. The cell voltage for the half-reaction will not change......greater amounts of the half reaction does not lead to greater voltages.

Sometimes the following formula is used: $E^o_{cell} = E^o_{red} + E^o_{ox}$

Determination of Spontaneity in Electrochemical Cells

- TSHCP are listed in a certain format.......the left-hand column are the oxidizing agents and the right-hand column are the reducing agents
- the strongest oxidizing agents are on top, the strongest reducing agents are on the bottom
- spontaneous reactions only occur when the oxidizing agent is above the reducing agent in the TSHCP
- to find if a reaction is spontaneous, simply determine if the oxidizing agent is above the reducing agent, if so, it is spontaneous...if not is not spontaeous

  Example: Predict if the following redox reaction is spontaneous:

  $Cu^{2+}(aq) + Zn(s) \rightarrowtail Cu(s) + Zn^{2+}(aq)$

  Answer: Cu^{2+} is the oxidizing agent, Zn is the reducing agent

  Since Cu^{2+} is above Zn then the reaction is spontaneous(check TSHCP)

Formation of Table of Redox Half-Reactions from Experimental Results

- Given a series of experimental results you can develop a table of half reactions listed in proper order of strength of oxidizing/reducing agents
- To accomplish this task, simply determine the oxidizing agents in the experimental evidence given, then list them in order of their strength.....use a process of deduction to determine the order
- Example: Develop a table of redox half-reactions from the given redox reactions. All reactions were observed to be spontaneous.

  $Fe(s) + H^{+}(aq) \rightarrowtail Fe^{3+}(aq) + H_2(g)$

  $Fe(s) + Cr^{3+}(aq) \rightarrowtail Fe^{3+}(aq) + Cr(s)$

  $Cu^{2+}(aq) + H_2(g) \rightarrowtail Cu(s) + H^{+}(g)$

  Answer: Identify the oxidizing agent in each reaction:

  H^{+}, Cr^{3+}, Cu^{2+}

  In terms of strength the order should be Cu^{2+}, H^{+} then Cr^{3+}

  **Do not forget that Fe is also present, but is being oxidized in both reactions, therefore, the oxidizing agent is Fe^{3+} which can also be placed. Remember that since Fe is the reducing agent in the reaction with chromium(III)ions, it is lower than the oxidizing agent, which makes Fe^{3+} half reaction last

  $Cu^{2+} + 2e^{-} \rightarrowtail Cu$

  $H^{+} + e^{-} \rightarrowtail H_2$

  $Cr^{3+} + 3e^{-} \rightarrowtail Cr$

  $Fe^{3+} + 3e^{-} \rightarrowtail Fe$

Redox Spontaneity Rule

A spontaneous redox reaction occurs only if the ***oxidizing agent is above the reducing agent*** in a table of redox half-reactions.

OA
+ ------------> Spontaneous reaction
RA

RA
+ -------------> Non-spontaneous reaction
OA

A spontaneous redox reaction in solution is one in which visible evidence is present in a few minutes.

Spontaneous reaction means that it occurs without any energy added to the system...non-spontaneous redox reactions can only occur if energy is provided.

Electrolysis

Historical Development

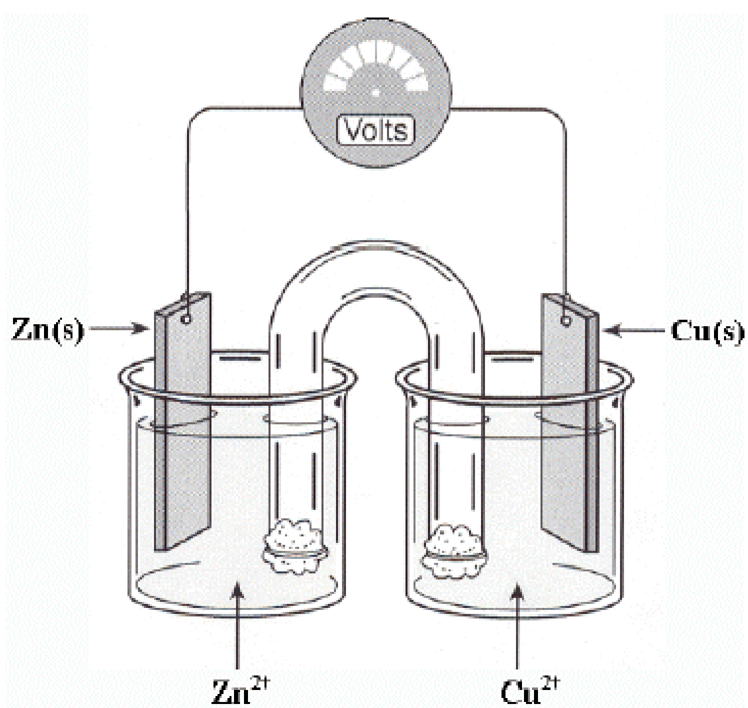
- Not all reactions are spontaneous. In fact, many reactions require energy to proceed. This was the focus of many chemists.
- Sir Humphry Davy attempted to electrolyze molten (liquid) sodium chloride. He produced two unknown substances which, upon further analysis, proved to be two new elements, sodium and chlorine. (Why would he not have used solid salt or aqueous salt?)
- From these beginnings chemistry eventually developed the practice of electroplating which is of huge importance in society and industry

Definitions		
	Electrolysis	Process of converting electrical energy to chemical energy
	Electrolytic Cell	A device that requires electrical energy to cause non-spontaneous redox reactions to occur
	Electroplating	The process whereby a metal is deposited (plated) onto the cathode in an electrolytic cell

Electrolytic Cells

- An electrolytic cell is very similar to an electrochemical cell. In fact, the only differences are:
  1. There must be a power supply (instead of a voltmeter/light/motor etc)
  2. The electrodes are opposite of electrochemical cells

- It can be drawn:



- An electrolytic cell contains the following elements:
  1. Anode (Oxidation occurs here)
  2. Cathode (Reduction occurs here)
  3. Salt bridge (Not always necessary)
  4. Power supply (Found between wires connecting electrodes)
  5. Direction of flow of electrons (from anode to cathode)

- cell notation cannot be used as in electrochemical cells.......however, a given cell notation for an electrochemical cell can be reversed to give the electrolytic cell

- Note: water can undergo electrolysis to produce the elements hydrogen and oxygen

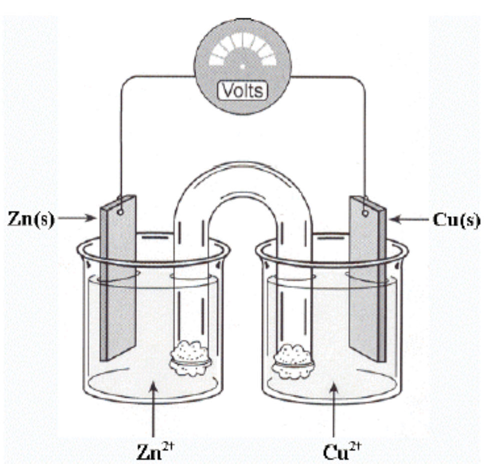
$$2H_2O(l) \rightarrow 2\ H_2(g) \quad + \quad O_2(g) \qquad E^o = -2.057\ V$$

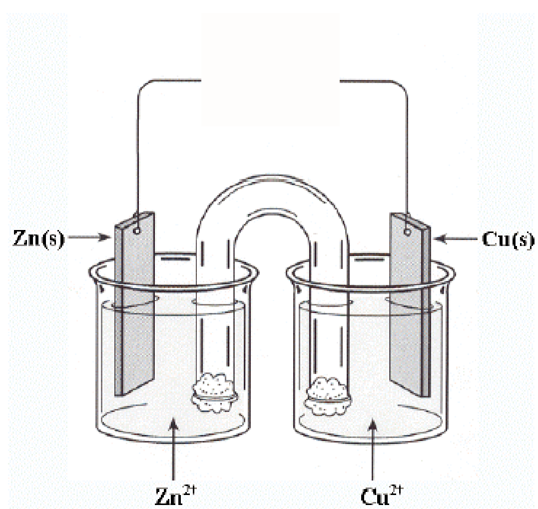
- When the anode is oxidized, it may or may not seem to disappear. If it does disappear, the metal atoms are being oxidized into ions that add to the electrolytic solution. However, it is very easy to notice when the cathode is being reduced. It becomes larger. It is being coated with pure metal (being reduced from the ionic form in solution). This is called electroplating.

- The process of electrolysis is very important. Galvanizing such things as nails (electroplating with zinc) allows it to resist corrosion (such as rust). Electroplating metals with chromium (chrome) also offers protection against corrosion (cars, etc). Metal alloys such as stainless steel contain metals that offer superior protection against corrosion (utensils, taps, sinks). In addition, metal purification uses this process to produce 99.99% pure metals.

- As in electrochemical cells, you must be able to predict the half-reactions that occur in the cell. Conversely, given the half-reactions you must write the equation for the electrolytic cell.

- Comparison of Electrolytic Cell vs Electrochemical Cell





	Electrolytic Cell	Electrochemical Cell
reaction	non-spontaneous	spontaneous
energy conversion	electric to chemical	chemical to electric
anode	+ve (copper)	-ve (zinc)
cathode	-ve (zinc)	+ve (copper)
reaction at anode (ox)	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
reaction at cathode (red)	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
cell reaction	$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
electrode behaviour	anode dissolves, cathode grows	anode dissolves, cathode grows
cell potential	negative	positive
efficiency	less	more
electron flow	anode to cathode	anode to cathode

Determination of Current Required for an Electrolytic Cell

- To determine the amount of voltage required for an electrolytic cell, the same procedure can be applied as an electrochemical cell. You will notice that the cell potential is negative. In fact, the actual voltage required will always be larger than the calculated value.
  For Example: The $Zn|Zn^{2+}\|Cu^{2+}|Cu$ cell produces 1.10V. To cause the non-spontaneous reaction to occur electrical energy in excess of this amount of energy is required (>1.10 V)......in fact, if a voltage of 2.00 V is applied to this cell only 0.90 V are available to do work.
- This fact makes electrochemical cells more efficient than electrolytic cells
- electron flow is still from anode to cathode, it is just that the anode and cathode are opposite of what they were in the electrochemical cell

Stoichiometry and Electroplating......Faraday's Law

- Michael Faraday determined that the number of moles of electrons which passes through an electrolytic cell is connected to the current applied to that cell over time.....Faraday's Law

The amount of a substance produced or consumed in an electrolysis reaction is directly proportional to the quantity of electricity that flows through the circuit.

- Faraday's constant is to electrons what molar volume is to gases

This can be expressed as the following formula:

$Q = nF$ where Q is the total charge
n is the number of moles of electrons
F is Faraday's constant (96 500 coulombs/mol) (data table)

- To correctly use this law, we must be able to calculate the total charge, Q. This can be done using the following formula (to better understand electricity):

$Q = It$ where Q is the total charge
I is the amount of current applied
t is the time over which the current is applied (in seconds)

These formulas can be combined:

Examples: Calculate the moles of Mg produced when a current of 60 Amps is passed through a magnesium chloride solution for 4.00 hours.

Answer: write out the given
I = 60 A
t = 4.00 h (change to seconds)
F = 96 500 C/mol

$$n = \frac{(60\text{A})(1.44 \times 10^4\ \text{s})}{96\ 500\ \text{C/mol}}$$

$n = 8.95$ mol e^-

This only gives us the mole of electrons, not the moles of magnesium.

To correctly calculate the mole of magnesium, write the half-reaction and use stoichiometry to determine the answer.

$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$$

$n_{mg} = n_e \times w/g$

$= 8.95$ mol e^- x (1 mol Mg/2 mol e^-)
= 4 mol Mg

* from here, the mass of magnesium could easily be found!

- There are many variations of these problems, you could be asked to find any of the variables time, mass, current or moles of electrons given the other variables.
- Example: 0.35 g of copper was plated onto the cathode in an electrolytic cell. The current applied during this process was 2.5 A. How much time did this process take?

Answer: rearrange the formulas to solve for time:

$t = n_e F/I$

F and I are know, however, n_e must be found.....use mass and the mole ratio to find it

$n_e = n_{Cu} \times w/g$
$= m/M \times w/g$
$= (0.35\ g/63.55\ g/mol) \times 2\ mol\ Cu\ e^-/1\ mol\ Cu$ ($Cu^{2+} + 2e^- \rightarrow Cu$)
$= 0.0110\ mol\ of\ Cu\ e^-$

$t = n_e F/I$
$= (0.0110\ mol\ Cu\ e^- \times 96\ 500\ C/mol\ Cu\ e^-) / 2.5\ A$
$= 4.25 \times 10^2\ s$

Outcomes should be checked when preparing for the public including those that are found in the last STSE (WARNING - BOREDOM WILL BE CERTAIN!)

1. Metallurgy
2. pyrometallurgy
3. hydrometallurgy
4. mineral
5. Ore
6. Flotation (and process)
7. Slag
8. Leaching
9. Purification of copper using electrolytic cell
10. Risk/benefit of pyrometallurgy
11. Electrowinning pure nickel from nickel(II)subsulfide
12. Which is better, pyro vs hyrometallurgy?

Batteries

Definition A set of galvanic cells connected in series (sometimes the set is only one!)

- There are two main types of batteries (cells), and many variations of each depending upon their application. In general:
  1. **Primary Batteries are not rechargeable**
  2. **Secondary Batteries are rechargeable**
- The most common examples of batteries you might find are:

A. Dry Cell
- ✓ galvanic cell
- ✓ electrolyte contained in a paste thickened with starch
- ✓ portable
- ✓ disposable
- ✓ stops working when reactants are used up
- ✓ zinc anode, inert graphite cathode
- ✓ cheap
- ✓ egflashlight, remote
- ✓ AAA, AA, C, D all 1.5-V

B. Alkaline Cell
- ✓ galvanic cell
- ✓ electrolyte contained in a paste thickened with KOH (hence the alkaline)
- ✓ portable
- ✓ disposable, if proper safety followed
- ✓ stops working when reactants used up
- ✓ zinc anode, inert graphite cathode
- ✓ more expensive BUT longer lasting
- ✓ eg many
- ✓ AAA, AA, C, D all 1.5-V

C. Button Cell
- ✓ galvanic cell
- ✓ electrolyte contained in paste thickened with KOH (hence alkaline as well)
- ✓ very portable
- ✓ disposable (unless if of mercury type)
- ✓ stops working when reactants used up
- ✓ zinc anode, stainless steel cathode
- ✓ very small, allows for many uses
- ✓ eg watches, pacemakers, hearing aids, tiny surgical instruments
- ✓ 2 types, either 1.3- or 1.6-V

D. Lead Storage
- ✓ combination of galvanic and electrolytic cell
- ✓ provides power when in use but must be recharged using electrical energy (when wheels in a car turn they turn a generator which reversed the galvanic process)
- ✓ lead anode, lead(IV)oxide cathode, both in an acid electrolyte
- ✓ not portable
- ✓ must be disposed of in proper manner
- ✓ can work for very long time since reactions replenish each other (however,

not 100% return so eventually it will run out of lead)

- ✓ many uses but safety is a factor (can break, leak conc acid a problem)
- ✓ eg skidoo, car atv
- ✓ works as a series of cells together, separated by spacers
- ✓ each cell voltage can be summed to determine total voltage
- ✓ common car battery is 6 x 2V = 12 V but many versions abound

E. Ni-Cd (nickel-cadmium)

- ✓ same as lead storage battery except very portable
- ✓ must be plugged into a charger to reverse reaction
- ✓ can work for a long time but typically wear out
- ✓ safety risk....the heavy metal cadmium is toxic and if thrown into dumps, it can enter the food chain (eventually) bad on humans
- ✓ typically 1.4-V
- ✓ still considered alkaline (electrolyte is KOH)

Fuel Cells (Hydrogen Cell) and the automobile

- Currently the internal combustion engine is one of the major causes of global warming, acid rain and other environmental problems (smog)
- Due to increasing public concerns and pressure, automobile manufacturers are attempting to develop alternative means of powering vehicles
- One attempt (mostly by Ballard Technologies of Canada) is focused on the hydrogen fuel cell
- this cell produces electricity (not heat) when reactants (hydrogen) are supplied, and produces water vapour which is environmentally friendly
- it is very efficient, compared to the combustion reaction which is very inefficient
  internal combustion $2H_2 + O_2 \rightarrow 2H_2O$ + heat (25% conversion)
  hydrogen fuel cell $2H_2 + O_2 \rightarrow 2H_2O$ + electricity(80% conversion)
- only problem, uncombined hydrogen is not found naturally on earth (by itself).....ballard is trying to produced hydrogen using electrolysis of water but has not perfected the process
- reactants continuously flow into the battery, thus is also called a flow battery
- fuel supply is unlimited
- it is an alkaline fuel cell (operates using KOH solution)
- also used by the space shuttle
- half reactions are:
  Cathode (reduction) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
  Anode (oxidation) $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ (x2)
  Overall reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- as you can observe, the products are water and if water can be converted to hydrogen and oxygen through electrolysis, the reaction can be neverending! However, electrolysis requires energy so an environmentally friendly source of energy must be found (possible solar) or the whole process is pointless.
- Diagram of a hydrogen fuel cell...note the inert carbon electrodes

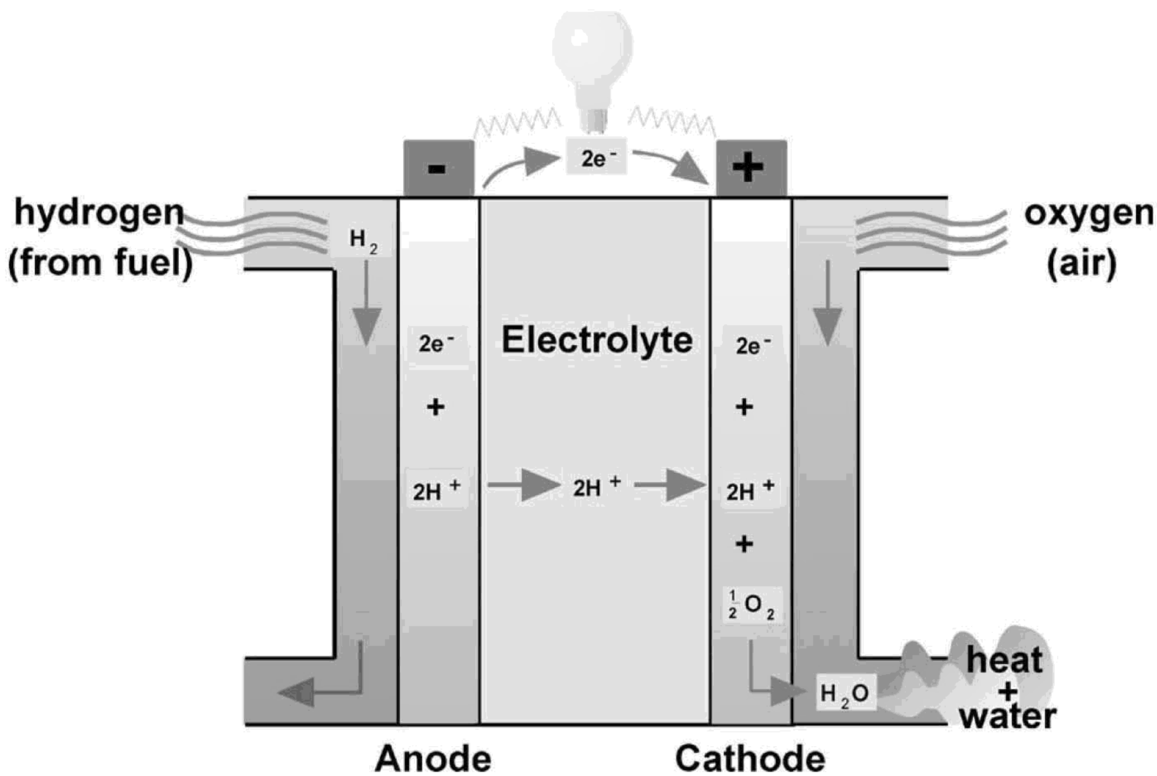


Fig. 2. Schematic of a PEM fuel cell operation. Source: World Fuel Cell Council.