

AP* Chemistry ELECTROCHEMISTRY

Terms to Know:

Electrochemistry – the study of the interchange of chemical and electrical energy **Voltaic** or **Galvanic Cell** – IS a battery but not a dry cell; *generates useful electrical energy* **Electrolytic Cell** – *requires useful electrical* energy to drive a thermodynamically unfavorable reaction **OIL RIG** – oxidation is loss, reduction is gain (of electrons)

Oxidation – the loss of electrons, increase in charge

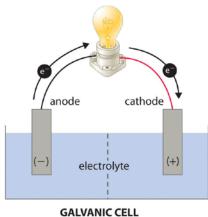
Reduction – the gain of electrons, reduction of charge

Oxidation number – the assigned charge on an atom

Electrochemistry Involves TWO MAIN TYPES Of Electrochemical Cells:

- 1. **Galvanic (voltaic) cells** which are thermodynamically favorable chemical reactions (battery)
- 2. **Electrolytic cells** which are thermodynamically unfavorable and require external e^- source (a direct current or DC power source)

BOTH of these fit into the category entitled **Electrochemical cells**



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:

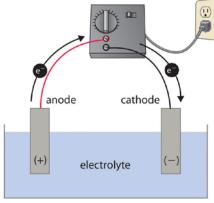
 $Y \rightarrow Y^+ + e^-$

Reduction half-reaction:

 $Z + e^- \rightarrow Z^-$

Overall cell reaction:

 $Y + Z \rightarrow Y^+ + Z^- (G < 0)$



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:

 $Z^- \rightarrow Z + e^-$

Reduction half-reaction:

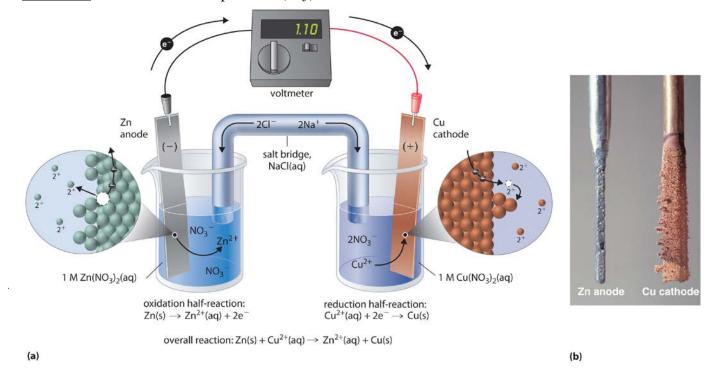
 $Y^+ + e^- \rightarrow Y$

Overall cell reaction:

 $Y^+ + Z^- \rightarrow Y + Z (G > 0)$

GALVANIC or VOLTAIC CELL "ANATOMY"

- <u>Anode</u> the electrode where oxidation occurs. After a period of time, the anode may appear to become smaller as it falls into solution. (Zn in our illustration below)
- <u>Cathode</u> the electrode where reduction occurs. After a period of time it may appear larger, due to ions from solution plating onto it. (Cu in our illustration below)
- <u>Inert electrodes</u> used when a gas is involved OR ion to ion involved such as Fe³⁺ being reduced to Fe²⁺ rather than Fe⁰; made of Pt (expensive) or graphite (cheap)
- <u>Salt bridge</u> used to maintain electrical neutrality in a galvanic cell; may be filled with agar which contains a neutral salt
- <u>Electron flow</u> ALWAYS through the wire from anode to cathode (alphabetical order)
- <u>Voltmeter</u> measures the cell potential (*emf*) in volts.



Examine the diagram above. Take note of the following mnemonic devices (easy ways to remember "stuff"): All of the following refer to the construction of a thermodynamically favorable cell – one that can act as a battery:

AN OX – oxidation occurs at the anode (may show mass decrease)

RED CAT – reduction occurs at the cathode (may show mass increase)

FAT CAT – The electrons in a voltaic or galvanic cell ALWAYS flow

From the Anode To the CAThode

Ca+hode – the cathode is + in galvanic (voltaic) cells, so it stands to reason the anode is negative **Salt Bridge** – bridge between cells whose purpose is **to provide ions to balance the charge**. Usually made of a salt filled agar (KNO₃) or a porous disk may be present instead.

EPA – in an electrolytic cell, there is a positive anode.

Galvanic cells involve oxidation-reduction or redox reactions. Balance this redox reaction:

 $MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$ [acidic]

RED:

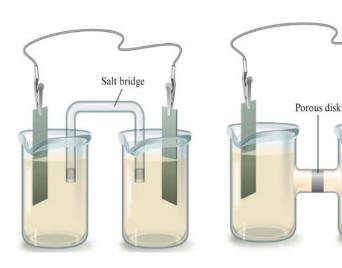
OX:

Overall rxn:



- If we place MnO₄⁻ and Fe²⁺ in the same container, the electrons are transferred directly when the reactants collide. No useful work is obtained from the chemical energy involved which is instead, released as heat!
- We can harness this energy if we separate the oxidizing agent from the reducing agent, thus requiring the e^- transfer to occur through a wire! We can harness the energy that way to run a motor, light a bulb, etc.
- Sustained electron flow cannot occur in the picture above.

Why not? As soon as electrons flow, a separation of charge occurs which in turn stops the flow of electrons. How do we fix it? Add a salt bridge or allow flow through a porous disk.



• <u>Salt Bridge</u> – its job is to balance the charge using an electrolyte [usually in a Ushaped tube filled with agar that has the salt dissolved into it before it gels]. It connects the two compartments, ions flow *from* it, AND it keeps each "cell" neutral.

Use KNO₃ as the salt when constructing your own diagram so that no precipitation occurs!

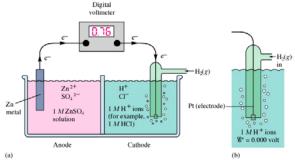
- porous disk or cup also allows both cells to remain neutral by allowing ions to flow
- <u>cell potential</u> E_{cell} , Emf, or ε_{cell} —it is a measure of the electromotive force or the "pull" of the electrons as they travel from the anode to the cathode [more on that later!]
 - volt (V) the unit of electrical potential; equal to 1 joule of work per coulomb of charge transferred
 - <u>voltmeter</u> measures electrical potential; some energy is lost as heat [resistance] which keeps the voltmeter reading a tad lower than the actual or calculated voltage. Digital voltmeters have less resistance. If you want to get picky and eliminate the error introduced by resistance, you attach a variable-external power source called a **potentiometer**. Adjust it so that zero current flows—the accurate voltage is then equal in magnitude but opposite in sign to the reading on the potentiometer.

Here's a nice animation from YouTube: http://www.youtube.com/watch?v=raOj8QGDkPA

ORIGIN OF STANDARD REDUCTION POTENTIALS

- Each half-reaction has a cell potential
- Each potential is measured against a standard, which is the standard hydrogen electrode [consists of a piece of inert Platinum that is bathed by hydrogen gas at 1 atm].

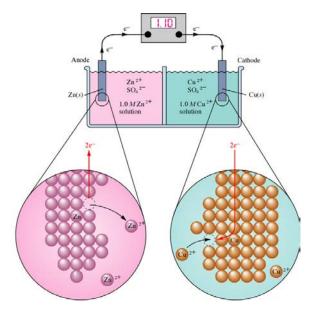
The hydrogen electrode is assigned a value of 0.00 V much like the isotope C-12 is assigned an atomic mass of exactly 12.000 amu and all other atomic masses are measured relative to it.



- standard conditions –1 atm for gases, 1.0M for solutions and 25°C for all (298 K)
- <u>naught</u>, o we use the *naught* to indicate standard conditions [Experiencing a thermo flashback?]

That means E_{cell} , Emf, or $\varepsilon_{\text{cell}}$ become E_{cell}° , Emf° , or $\varepsilon_{\text{cell}}^{\circ}$ when measurements are taken at standard conditions. You'll soon learn how these change when the conditions are non-standard!

- The diagram to the right illustrates what really happens when a Galvanic cell is constructed from zinc sulfate and copper(II) sulfate using the respective metals as electrodes.
 - Notice that 1.0 M solutions of each salt are used
 - Notice an overall voltage of 1.10 V for the process



So, how do we construct a fully functional Galvanic or Voltaic cell?

First, we must make wise choices depending on materials available and cost. Knowing how to choose wisely is our next lesson! We need to interpret the data given on the table of standard reduction potentials as we engineer our Galvanic or Voltaic cell.

Interpreting a Table of Standard Electrode Potentials

- Figure Elements that have the most positive reduction potentials are easily reduced (in general, non-metals)
- Elements that have the least positive reduction potentials are easily oxidized (in general, metals)
- The reduction potential table can also be used as an activity series. Metals having less positive reduction potentials are more active and will replace metals with more positive potentials.

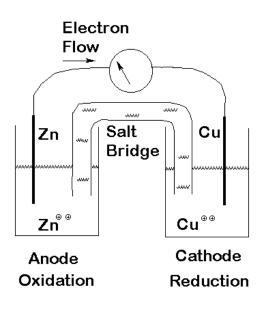
Let the engineering begin! The MORE POSITIVE reduction potential gets to indeed be reduced IF you are trying to set up a cell that can act as a galvanic or voltaic cell (a battery in other words).

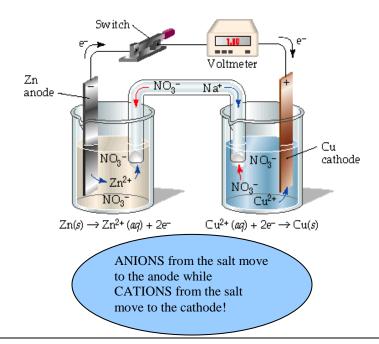
There once was a table of reduction potentials in the reference tables of the AP Chemistry exam. Currently, we expect the data will be given in either a small table or simply embedded within the text of the question. For your homework, you'll need to consult a table similar to this one.

Half-reaction	\mathscr{E}° (V)	Half-reaction	& (A
$f_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^{-} \rightarrow Ag^{+}$	1.99	$Cu^{2+} + 2e^{-} \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.2
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.2
$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.2
$bO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^{-} \rightarrow Cu^{+}$	0.1
$\text{InO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.0
$O_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^{-} \rightarrow Fe$	-0.0
$4 \text{nO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2 \text{O}$	1.51	$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.1
$u^{3+} + 3e^{-} \rightarrow Au$	1.50	$Sn^{2+} + 2e^{-} \rightarrow Sn$	-0.1
$bO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.2
$l_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.3
${\rm r_2O_7}^{2-} + 14{\rm H}^+ + 6{\rm e}^- \rightarrow 2{\rm Cr}^{3+} + 7{\rm H_2O}$	1.33	$Cd^{2+} + 2e^{-} \rightarrow Cd$	-0.4
$0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.4
$InO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.5
$O_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^{-} \rightarrow Cr$	-0.7
$r_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.7
$O_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.8
.uCl ₄ [−] + 3e [−] → Au + 4Cl [−]	0.99	$Mn^{2+} + 2e^{-} \rightarrow Mn$	-1.1
$IO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^{-} \rightarrow Al$	-1.6
$lO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.2
$Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^{-} \rightarrow Mg$	-2.3
$g^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^{-} \rightarrow La$	-2.3
$(g_2^{2+} + 2e^- \rightarrow 2Hg)$	0.80	$Na^+ + e^- \rightarrow Na$	-2.7
$e^{3+} + e^{-} \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^{-} \rightarrow Ca$	-2.7
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^{-} \rightarrow Ba$	-2.9
$InO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56		-2.9
$_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.0

Calculating Standard Cell Potential Symbolized by E°_{cell} OR Emf° OR $\varepsilon_{cell}^{\circ}$ [I'll mix and match!]

- Decide which element is oxidized or reduced using the table of reduction potentials. Once again,
 <u>THE Metal with the MORE POSITIVE REDUCTION POTENITAL gets to be REDUCED</u>.
 So, it stands to reason that the other metal is oxidized!
- 2. Write both equations AS IS from the chart with their associated voltages.
- 3. Reverse the equation that will be oxidized and change the sign of its voltage [this is now $E^{\circ}_{\text{oxidation}}$]
- 4. Balance the two half reactions **do not multiply voltage values** Why not? A volt is equivalent to a J/coulomb or $\frac{J}{c}$ which is a ratio.
- 5. Add the two half reactions and the voltages together.
- 6. $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$ o means standard conditions: 1atm, 1M, 25°C





Exercise 1

a. Consider a galvanic cell based on the reaction

$$\mathrm{Al}^{3+}(aq) + \mathrm{Mg}(s) \rightarrow \mathrm{Al}(s) + \mathrm{Mg}^{2+}(aq)$$

Give the balanced cell reaction and calculate E° for the cell.

b. A galvanic cell is based on the reaction [you'll need a more complete table of reduction potentials!]

$$MnO_4^-(aq) + H^+(aq) + ClO_3^-(aq) \rightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$

Give the balanced cell reaction and calculate E° for the cell.

A: 0.71 V B: 0.32 V

Exercise 2

Calculate the cell voltage for the galvanic cell that would utilize silver metal and involve iron(II) ion and iron(III) ion. Draw a diagram of the galvanic cell for the reaction and label completely.

 $E^{\circ}_{\text{cell}} = 0.03 \text{ V}$

CELL POTENTIAL, ELECTRICAL WORK & FREE ENERGY

It is time to combine the thermodynamics and the electrochemistry, not to mention a wee bit of physics.

• The *work* that can be accomplished when electrons are transferred through a wire depends on the "push" or *emf* which is defined in terms of a potential difference [in volts] between two points in the circuit.

$$emf(V) = \varepsilon = \frac{work(J)}{charge(C)}$$

- Thus one joule of work is produced [or required] when one coulomb of charge is transferred between two points in the circuit that differ by a potential of one volt
 - IF work flows OUT of the system, it is assigned a MINUS sign (makes sense since Joules were LOST)
 - When a cell produces a current, the cell potential is positive and the current can be used to *do* work THEREFORE ε and work have opposite signs!

$$\varepsilon = -\frac{work(\mathbf{J})}{charge(\mathbf{C})} = \frac{-w}{q} : -w = \varepsilon q$$

- ightharpoonup faraday(F)—the charge on one MOLE of electrons = 96,485 coulombs (Think 96,500 when answering multiple choice questions)
- \Rightarrow q = # moles of electrons $\times F$
- For a process carried out at constant temperature and pressure, w_{max} [neglecting the very small amount of energy that is lost as friction or heat] is equal to ΔG , therefore....

$$\Delta G^{0} = -nFE^{0}$$

G = Gibb's free energy

n = number of moles of electrons

 $F = \text{Faraday constant } 96,485 \frac{\text{J}}{\text{V} \cdot \text{mol}}$

So, it follows that:

- $-E^{o}$ implies thermodynamically unfavorable.
- $+E^{o}$ implies thermodynamically favorable (would be a good battery!)

Exercise 3

Using the table of standard reduction potentials, calculate ΔG° for the reaction

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

Explain whether or not this reaction is thermodynamically favorable.

Exercise 4

Using the table of standard reduction potentials, predict whether $1 M \text{ HNO}_3$ will dissolve gold metal to form a $1 M \text{ Au}^{3+}$ solution.

= no

DEPENDENCE OF CELL POTENTIAL ON CONCENTRATION

Voltaic cells at NONstandard conditions: LeChatlier's principle can be applied. An increase in the concentration of a reactant will favor the forward reaction and the cell potential will increase. The converse is also true!

Exercise 5

For the cell reaction

$$2Al(s) + 3Mn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Mn(s)$$
 $E^{\circ}_{cell} =$

predict whether E_{cell} is larger or smaller than E°_{cell} for the following cases and justify your answer.

a.
$$[Al^{3+}] = 2.0 M$$
, $[Mn^{2+}] = 1.0 M$

b. $[Al^{3+}] = 1.0 M, [Mn^{2+}] = 3.0 M$

a. smaller b. larger

NMSI Disclaimer: The curriculum framework for the course excludes the quantitative treatment of the Nernst Equation, but we feel it is in the best interest of the student to learn this concept for two reasons:

- It makes students more college ready, especially the students that will earn a qualifying score and obtain full credit for the university course.
- 2) At least half of the students in any given AP Chemistry course are mathematically inclined and may actually understand a concept better through the *application* of the mathematics of *Q* and how it relates back to LeChâtelier's Principle.

For a more quantitative approach at nonstandard conditions use the **Nernst Equation**:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

 $R = \text{Gas constant } 8.315 \text{ J/K} \bullet \text{ mol}$

F =Faraday constant

$$Q = \text{reaction quotient} = \frac{\left[\text{products}\right]^{coefficient}}{\left[\text{reactants}\right]^{coefficient}}$$

E = Energy produced by reaction

T = Temperature in Kelvins

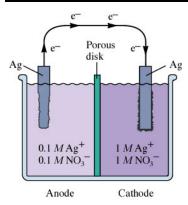
n = # of electrons exchanged in BALANCED redox equation

Rearranged, another useful form

NERNST EQUATION:
$$E = E^{\circ} - \frac{0.0592}{n} \log Q$$
 @ 25°C (298K)

As E declines with reactants being converted into products, E eventually reaches zero.

Zero potential means reaction is at equilibrium [dead battery]. Also note, Q = K AND $\Delta G = 0$ as well.



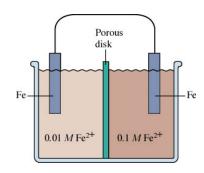
CONCENTRATION CELLS

We can construct a cell where both compartments contain the same components BUT at different concentrations

Notice the difference in the concentrations pictured at left. Because the right compartment contains $1.0 M \text{ Ag}^+$ and the left compartment contains $0.10 M \text{ Ag}^+$, there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves [producing Ag^+ ions] to raise the concentration of Ag^+ in solution.

Exercise 6

Determine the direction of electron flow and designate the anode and cathode for the cell represented here.

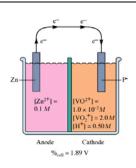


left → right

Exercise 7

Determine E^{o}_{cell} and E_{cell} based on the following half-reactions:

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$
 $E^\circ = 1.00 \text{ V}$
 $Zn^{2+} + 2e^- \rightarrow Zn$ $E^\circ = -0.76\text{V}$



Where,

$$T = 25^{\circ}\text{C}$$

 $[\text{VO}_2^+] = 2.0 \text{ M}$
 $[\text{H}^+] = 0.50 \text{ M}$

$$[VO^{2+}] = 1.0 \times 10^{-2} M$$

$$[Zn^{2+}] = 1.0 \times 10^{-1} M$$

 $E_{\text{cell}}^{\text{o}} = 1.76 \text{ V}$ $E_{\text{cell}} = 1.89 \text{ V}$

SUMMARY OF GIBB'S FREE ENERGY AND CELLS

- \mathcal{F} – E^{o} implies thermodynamically unfavorable.
- F + E^0 implies thermodynamically favorable (would be a good battery!)
- E = 0, equilibrium reached (dead battery)
- relarger the voltage, more thermodynamically favorable the reaction
- $rightharpoonup \Delta G$ will be negative in thermodynamically favorable reactions
- $\mathcal{F} K > 1$ are favored

Two important equations:

 $\Delta G = -nFE^{\circ}$ ["minus nunfe"] $\Delta G = -RT \ln K$ ["ratlink"]

G = Gibbs free energy [Reaction is thermodynamically favorable if ΔG is negative]

n = number of moles of electrons.

 $F = \text{Faraday constant } 9.6485 \times 10^4 \text{ J/V} \text{ (1 mol of electrons carries } 96,485 \text{ C} \text{)}$

E = cell potential

 $R = 8.31 \text{ J/mol} \bullet \text{K}$

T =Kelvin temperature

 $K = \text{equilibrium constant [products]}^{\text{coeff.}} / [\text{reactants}]^{\text{coeff}}$

Favored conditions: $E_{cell} > 0$ K > 1 $\Delta G < 0$

Exercise 8

 $S_4O_6^{2-}(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$ For the oxidation-reduction reaction

The appropriate half-reactions are

$$S_4O_6^{2^-} + 2 e^- \rightarrow 2 S_2O_3^{2^-}$$
 $E^{\circ} = 0.17V$
 $Cr^{3^+} + e^- \rightarrow Cr^{2^+}$ $E^{\circ} = -0.50 V$

Balance the redox reaction, and calculate E° and K (at 25°C).

 $E^{\circ} = 0.67 \text{ V}$ $K = e^{52.2} = 4.8 \times 10^{22}$

Applications of Galvanic Cells

Batteries: cells connected in series; potentials add together to give a total voltage Examples:

Lead-storage batteries (car): Pb anode, PbO₂ cathode, H₂SO₄ electrolyte Dry cell batteries

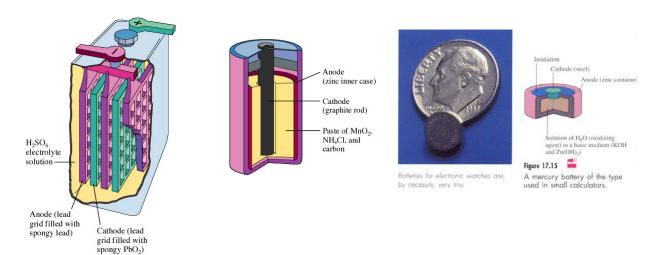
Acid versions: Zn anode, C cathode; MnO₂ and NH₄Cl paste

Alkaline versions: some type of basic paste, ex. KOH

Nickel-cadmium – anode and cathode can be recharged

Fuel cells

Reactants continuously supplied (spacecraft –hydrogen and oxygen)



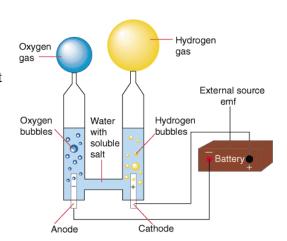
ELECTROLYSIS AND ELECTROLYTIC CELLS

Electrolysis involves the application of an electric current to bring about chemical change. Literal translation "split with electricity".

$$2H_2O(aq)$$
 + electrical energy $\rightarrow 2H_2(g) + O_2(g)$

Electrolytic cells [thermodynamically unfavorable cells]:

- Used to separate ores or plate out metals.
- Timportant differences between a voltaic cells and electrolytic cells:

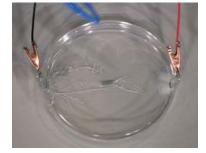


- 1. Voltaic cells are *thermodynamically favorable* and electrolytic cells are NOT and are thus forced to occur by using an electron pump or battery or any type of DC source.
- 2. A voltaic cell is separated into two half cells to generate electricity; an electrolytic cell occurs in a single container.
- 3. A voltaic [or galvanic] cell IS a battery, an electrolytic cell NEEDS a battery
- 4. AN OX and RED CAT still apply BUT the polarity of the electrodes is reversed. The cathode is Negative and the anode is Positive (remember **E.P.A electrolytic positive anode**). However, electrons still flow FATCAT.
- 5. Electrolytic cells usually use inert electrodes (Pt or graphite for example)

We can also use electrolysis to recover metals from solution through the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

This picture shows a Petri dish containing a solution of tin(II) chloride with alligator clips attached to paper clips that are submerged into the solution.

The net ionic reaction is: $SnCl_2(aq) \rightarrow Sn(s) + 2Cl^{-}(aq)$



Predicting the Products of Electrolysis:

If there is no water present and you have a pure molten ionic compound, then:

The cation will be reduced (gain electrons/go down in charge)

The anion will be oxidized (lose electrons/go up in charge)

If water is present and you have an aqueous solution of the ionic compound, then:

you'll need to figure out if the ions are reacting or the water is reacting.

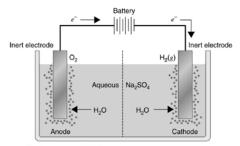
you can always look at a reduction potential table to figure it out but, as a rule of thumb:

To group IA or IIA metal will be reduced in an aqueous solution

- water will be reduced instead

representation of no polyatomic will be oxidized in an aqueous solution

water will be oxidized instead



Half Reactions for the electrolysis of water (no need to memorize)

If Oxidized: $2 \text{ H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{ H}^+ + 4 \text{ e}^-$

If Reduced: $2 \text{ H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$

CALCULATING THE ELECTRICAL ENERGY OF ELECTROLYSIS

There are basically only two questions we can ask about electrolysis on the AP Chemistry exam so, this may be viewed as "good news"!

How many grams of metal could be plated out if the time and amount of electrical current measured in amps are given?

How long would it take to plate out a given mass of metal if the current is given in amps?

Faraday's Law: The amount of a substance being oxidized or reduced at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell. This is great news since direct proportions lead to simple mathematical equations or formulas for us to employ!

Use dimensional analysis for these calculations, remembering: # **coulombs** = It

Think of these relationships as tools for your problem solving toolbox:

- 1 Volt = 1 Joule/Coulomb or you may prefer $1\frac{J}{c}$
- 1 Amp = 1 Coulomb/second or you may prefer $1\frac{c}{s}$, either way, it's a rate of the flow of charge (Note: The unit for current is amp, but symbolized by *I* for "inductance")
- **1 Faraday** = **96,485 Coulombs/mole of electrons** or you may prefer $96,485 \frac{c}{\text{mole of } e^-}$ Luckily, the balanced redox equation gives #moles of e^- /mole of substance and MM gives the number of grams/mole

Exercise 9

How long must a current of 5.00 A be applied to a solution of Ag⁺ to produce 10.5 g silver metal?

 $= 31.3 \min$

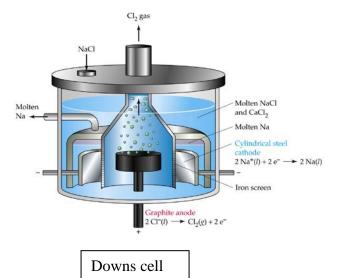
Exercise 10

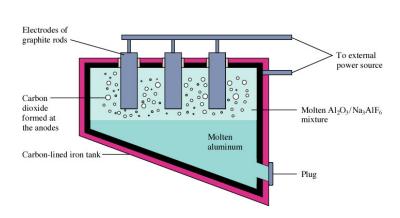
An acidic solution contains the ions Ce^{4+} , VO_2^+ , and Fe^{3+} . Using the E° values listed in Table 17.1 [Zumdahl], give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.

 $Ce^{4+} > VO_2^+ > Fe^{3+}$

APPLICATIONS OF ELECTROLYTIC CELLS

The most important is the production of pure forms of elements from mined ores which include purifying copper for use in wiring, producing aluminum from Hall-Heroult process, and separating sodium and chlorine using a Downs cell.





Hall-Heroult process for producing Aluminum

A counter argument can be made for stating that the most importing application of electrolytic cells involves electroplating which applies a thin layer of an expensive metal to a less expensive one for structural or cosmetic reasons. Pure gold is 24 carat and very soft, thus 24-carat gold rings would bend easily, thus a stronger structure metal is electroplated with gold to produce a sturdy version of a gold ring. If you see a car with a chrome bumper, it has also been electroplated.

Nature has a way of returning metals to their natural states, which is often their ore. We call this process corrosion. It involves the oxidation of the metal, which causes it to lose its structural integrity and attractiveness.

This is particularly troublesome when steel corrodes. The main component of steel is iron and about 20% of the iron and steel produced annually is used to replace rusted metal!

You are more familiar with the products resulting from oxidizing metal than you may think! You may even know the names of the thin oxide coating that may also server to protect metals. Ever heard of patina, tarnish, rust, etc.?

Can we combat this corrosion? Occasionally. For instance, ship hulls often have bars of titanium attached to them since Ti in salt water acts as the anode and is oxidized *instead* of the steel hull extending the life of the vessel. Additionally, Titanium is also immune to microbiologically influenced corrosion.