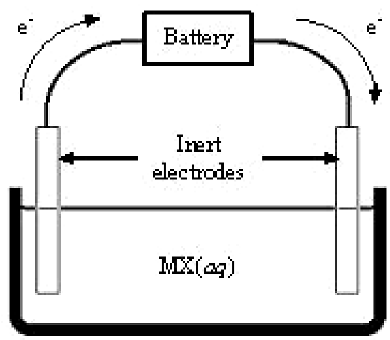
Name ___________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 27. Electrolytic Cells

(Reference: 21.7 Silberberg *5th edition*)

If an element doesn't occur naturally, where does a sample of it come from?

The Model: A Battery Used as an "Electron Pump"



If a battery is used to "pump" electrons from one electrode to a second electrode, it is possible to force a non-spontaneous reaction to occur. Let us at the moment consider an **electrolytic cell** that has inert electrodes. An inert electrode is made of some electrically-conducting substance, which is resistive to being oxidized or reduced. Graphite or an unreactive metal, like gold or platinum, may be used. In the cell to the right, the electrodes are submerged in an aqueous solution of some soluble salt, a strong electrolyte. (While the salt is represented generically as "MX", nothing is implied about the charges of the cation and anion—their charges do not have to be 1:1.)

Key Questions

1. As the battery pumps electrons from the electrode on the left to the electrode on the right, what charge begins to accumulate on each electrode? (Circle your choices.)

   Electrode on left: positive or negative **Electrode on right**: positive or negative

2. What species flows to the electrode on the left? to the electrode on the right? *Hints*: Do like charges attract or repel? Do opposite charges attract or repel? (Circle your choices.)

   Electrode on left: anions or cations **Electrode on right**: anions or cations

3. In each of the following half-reactions, are electrons reactants or products?

   Oxidation: e^- is reactant or product **Reduction**: e^- is reactant or product

4. In the electrolytic cell, which species are likely to be oxidized? to be reduced? (*Circle all choices that apply.*)

   Species likely to collide with anode and be oxidized: anions cations water

   Species likely to collide with cathode and be reduced: anions cations water

5 a. Now consider the **electrolysis** of $Na_2SO_4(aq)$ using inert electrodes exposed to the air. At the anode, either sulfate or water may oxidize:

$$2\ SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2\ e^- \qquad E^o_{ox} = -2.00\ V$$

$$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^- \qquad E^o_{ox} = -1.23\ V$$

Which species would you predict is the one that is oxidized at the anode? *Briefly explain why*.

b. When $Na_2SO_4(aq)$ is electrolyzed, either sodium cations or water may be reduced:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^o_{red} = -2.71\ V$$

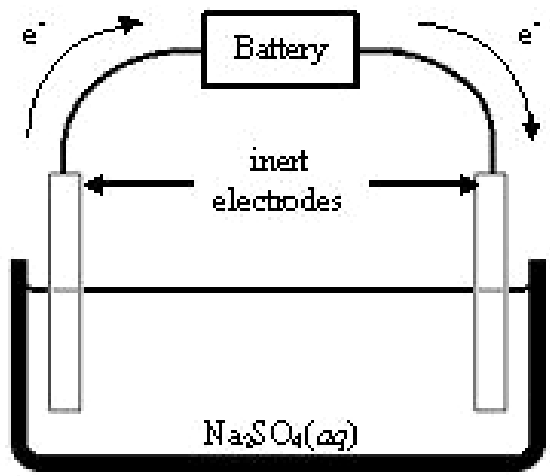
$$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq) \qquad E^o_{red} = -0.83\ V$$

Which species would you predict is the one that is reduced at the cathode? *Briefly explain why*.

c. Suppose $Na_2SO_4(aq)$ is electrolyzed using inert electrodes which are exposed to the air. On the following schematic of the electrolytic cell…

i. draw what is being consumed and what is being produced at each of the electrodes.

ii. draw arrows indicating the flow of each reactant and product.



d. Why cannot pure water be electrolyzed? (*i.e.*, Why must sodium sulfate or some similar electrolyte be dissolved in the water? *Hint*: Consider the flow of ions in the aqueous solution between the electrodes.)

6. Let us now consider the electrolysis of $CuSO_4(aq)$ using inert electrodes exposed to the air. The possible processes at the electrodes are:

at the anode		**at the cathode**	
$2\ SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2\ e^-$	$E^o_{ox} = -2.00$ V	$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	$E^o_{red} = 0.34$ V
$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$	$E^o_{ox} = -1.23$ V	$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	$E^o_{red} = -0.83$ V

a. Circle the half-reaction that occurs at the anode and the reaction at the cathode.

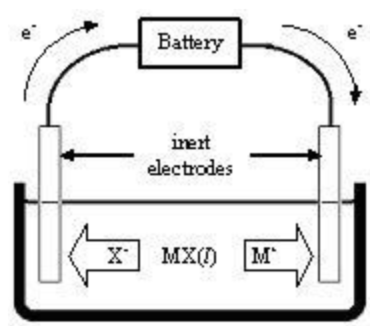
b. Write the overall cell reaction and determine the *absolute minimum* voltage that the battery must have to force this nonspontaneous reaction to occur. (I've said "absolute minimum," because ordinarily an additional voltage known as an **overvoltage** (a.k.a. over potential or junction potential) must be supplied to overcome the slow reaction kinetics due to the high activation energy required for gases to form at the electrode—*overvoltages vary, but are about 0.4 to 0.6 V for O_2 and H_2*.

- Overall reaction: ______________________________
- Minimum E^o_{cell} = ______________________________

c. If overvoltage is considered, what's the approximate E^o_{cell} ? E^o_{cell} = ______________

The Model: Electrolysis of Molten Salt

If we want to avoid the possibility of more than one half-reaction taking place at each electrode, the best way to do that is to limit which species can interact with the anode and cathode. Suppose instead of an aqueous solution of a salt (again, generically represented as "MX") we electrolyze the ***molten* salt** [*i.e.*, "MX(*l*)"]. Then it is possible that both the cations of the salt would be reduced to the elemental state at the cathode and the anions of the salt would be oxidized to the elemental state at the anode.



Key Questions

7. Why must a salt be in the liquid state if it is to be electrolyzed?

8 a. What is an advantage of electrolyzing a molten salt over electrolyzing an aqueous solution of that salt?

b. What is a procedural challenge to electrolyzing a molten salt?

9. Elemental magnesium does not occur freely in Nature, but Mg^{2+} is the third most abundant ion in sea water. At a concentration of 0.056 *M*, there is a virtually inexhaustible supply of magnesium in our oceans! Once magnesium chloride salt is isolated from sea water, it can be electrolyzed to yield magnesium metal. The light-weight magnesium metal is moderately strong, so it is a useful metal for construction (*e.g.*, of airplanes). The combustion of magnesium metal produces an intense light, so it is also used in pyrotechnics.

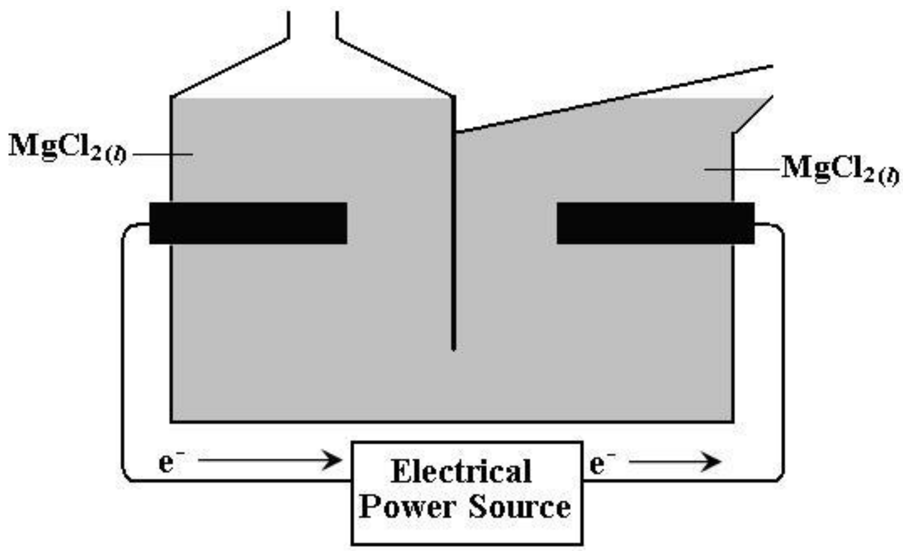
   a. Write the oxidation and reduction half-reactions that occur at the anode and cathode, respectively, when $MgCl_2(l)$ is electrolyzed using inert electrodes.

   Half reaction at anode: ______________________________________

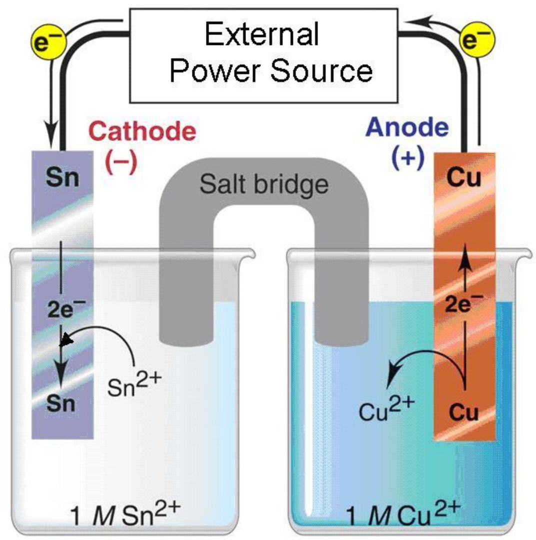
   Half reaction at cathode: ____________________________________

   b. Elemental magnesium metal, Mg, and chlorine gas, Cl_2, react explosively with each other! So when $MgCl_2(l)$ is electrolyzed, the products must be prevented from recombining. Use the design of the electrolytic cell to the right and the following physical data to explain how these elements may be collected when molten magnesium chloride, $MgCl_2(l)$, is electrolyzed using inert electrodes.

	T_f (°C)	*d* (g/mL)
Mg	649	1.7
$MgCl_2$	714	2.3



The Model: Electroplating



Electroplating is the process of using electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material (e.g. such as a metal). Electroplating is primarily used for depositing a layer of material to give it a desired property (e.g., abrasion and wear resistance, corrosion protection, aesthetic qualities, etc.) to a surface that otherwise lacks that property.

Another application uses electroplating to build up thickness on undersized parts as seen in the **electrolytic cell** to the right where an external power source is used to increase the thickness of the tin cathode.

Key Questions

10. The possible processes at the electrodes are:

at the cathode		at the anode	
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$E^o_{red} = -0.14$ V	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$E^o_{ox} = -0.34$ V
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	$E^o_{red} = -0.83$ V	$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$	$E^o_{ox} = -1.23$ V

a. Circle the half-reaction that occurs at the cathode and the half-reaction at the anode if the voltage is kept "low." (Water will *also* react if the voltage is high enough.)

b. Write the overall cell reaction and determine *minimum* voltage that the battery must have to force this nonspontaneous reaction to occur. (Do not consider overvoltage since gases are not involved.)

<u>Overall reaction</u>: ____

Minimum E^o_{cell} = ____

c. If water were to react at <u>*each*</u> electrode, what is the *minimum* voltage the battery must have for water to under go hydrolysis and produce hydrogen gas at the cathode and oxygen gas at the anode? (Since gases are involved <u>*remember to consider overvoltage*</u>) What is the net reaction involving water at each electrode?

<u>Overall reaction</u>: ____

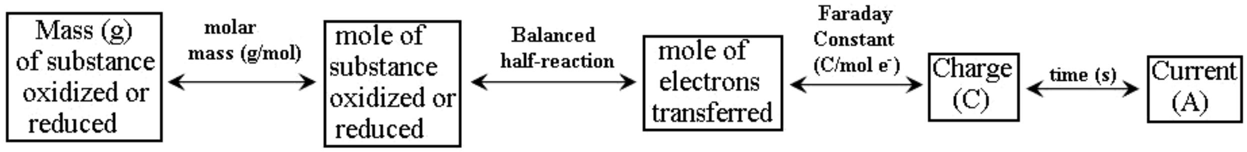
Minimum E^o_{cell} for the hydrolysis of water = ______________________________

d. What is the <u>*minimum*</u> voltage (<u>*remember to consider overvoltage*</u>) the battery must have for both hydrogen gas to form (but no O_2 at the anode) <u>*and*</u> tin to plate on the cathode?

The Model: Calculating the Mass of Metal Electroplated

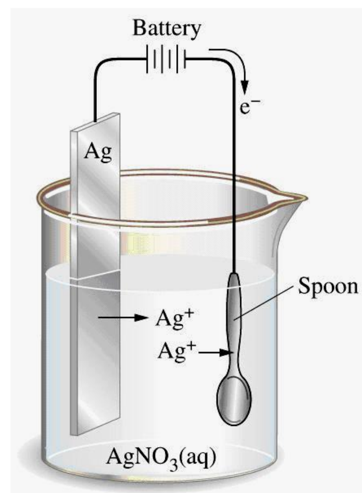
A common method of electroplating is achieved using the object to be electroplated as the cathode (e.g. the spoon in the figure below) and use as the anode the metal to be plated (e.g. silver) both submerged in an aqueous solution containing the ions to be plated (e.g. $AgNO_{3(aq)}$).

In the figure below, silver anode is oxidized ($Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + e^{-}$) and at the cathode Ag^{+} is reduced ($Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$). Thus there is no net reaction. The overall process consists of simply moving silver atoms from one electrode to the other. Since this is not a spontaneous process, an electrical current is needed to drive the process. The mass in grams of silver electroplated on the spoon is calculated using the following relationships:



The approximate mass of silver electroplated can be calculated from the electrical current in amps and the amount of time the current ran:

Current: 7.50 amps at a minimum of 0.80 V
Time: 30.0 minutes



<u>Useful Info. Needed to Calculate the Mass of Ag Electroplated</u>:

- 1 ampere (A) = 1 Coulomb per sec: **1 A = 1 C / s**
- Charge of 1 mol of electrons =96,485 C = 1 Faraday
  1 F = 96,485 C / 1 mol e-
- Ag^{+} (*aq*) + $e^{-} \rightarrow$ Ag (*s*) $E^{o}_{red} = 0.80$ V
  - Hence, 1 mol of electrons will plate 1 mol of Ag
- Molar Mass of Ag: 107.9 g/mol

Key Question

11. If the electrolytic cell above were run at 7.50 A for 30.0 minutes, <u>*use dimensional analysis*</u> to show that the maximum mass of silver that can be electroplated is 15.1 g.

12. How long will it take (in hours) to electroplate 40.0 g of Chromium onto a small automotive accessory from an aqueous $Cr(NO_3)_3$ solution using a current of 12 amps?
Cr = 51.0 g/mol. <u>*Use dimensional analysis to show your work*</u>.

Exercises

13. Zinc plating (galvanizing) is an important means of corrosion protection. Although the process is done customarily by dipping the object into molten zinc, the metal can also be electroplated from an aqueous Zn^{2+} solution. How many grams of zinc can be deposited on a steel tank from a $ZnSO_4$ solution when a 0.755 amp current flows for 2.00 days? *Use dimensional analysis to show your work*.

14. Electrolysis of molten NaCl is the major means of producing sodium metal. If 215 g of Na metal forms… *Use dimensional analysis to show your work and circle your answers*.
    a. How many moles of electrons are required?

    b. How many coulombs are required?

    c. How many amps are required to produce this amount in 9.5 hr?

15. In the electrolysis of a molten mixture of CsBr and $SrCl_2$, use your knowledge of periodic trends in ionization energy and electron affinity to identify the product that forms at the negative electrode (cathode) and at the positive electrode (anode). *Explain your reasoning*.

    Substance formed at the cathode: ______ *Reasoning:*

    Substance formed at the anode: ______ *Reasoning:*