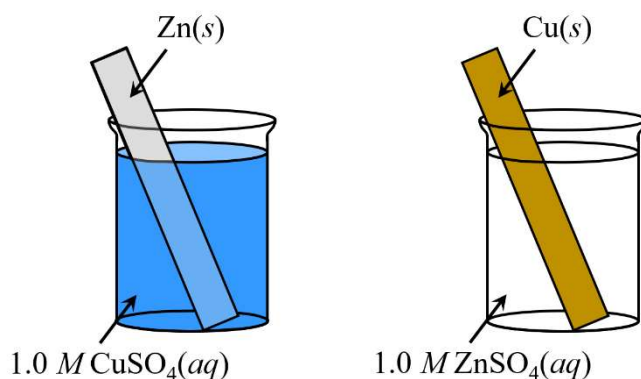


## 9.7 Galvanic (Voltaic) and Electrolytic Cells

Essential knowledge statements from the AP Chemistry CED:

- Each component of an electrochemical cell (electrodes, solutions in the half-cells, salt bridge, voltage/current measuring device) plays a specific role in the overall functioning of the cell. The operational characteristics of the cell (galvanic vs. electrolytic, direction of electron flow, reactions occurring in each half-cell, change in electrode mass, evolution of a gas at an electrode, ion flow through the salt bridge) can be described at both the macroscopic and particulate levels.
- Galvanic, sometimes called voltaic, cells involve a thermodynamically favored reaction, whereas electrolytic cells involve a thermodynamically unfavored reaction. Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and in what direction current flows.
- For all electrochemical cells, oxidation occurs at the anode and reduction occurs at the cathode.



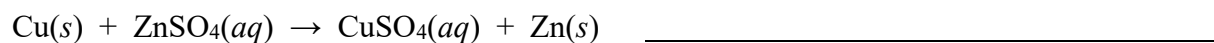
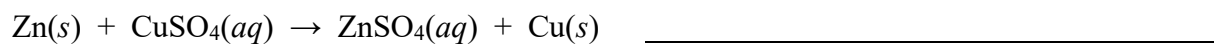
You can watch a short video of this reaction by scanning the QR code shown below.



1. A student places a strip of zinc metal into a solution of  $1.0\text{ M}$  copper(II) sulfate. The student also places a strip of copper metal into a solution of  $1.0\text{ M}$  zinc sulfate. The student's observations are shown in the table below.

Experiment	Observations
$\text{Zn}(s)$ placed in $\text{CuSO}_4(aq)$	A dark solid appears on the surface of the $\text{Zn}(s)$ . The color of $\text{CuSO}_4(aq)$ changes from dark blue to light blue.
$\text{Cu}(s)$ placed in $\text{ZnSO}_4(aq)$	The appearances of both $\text{Cu}(s)$ and $\text{ZnSO}_4(aq)$ remain unchanged.

- (a) Based on the results of this experiment, classify each of the following reactions as thermodynamically favored or unfavored.

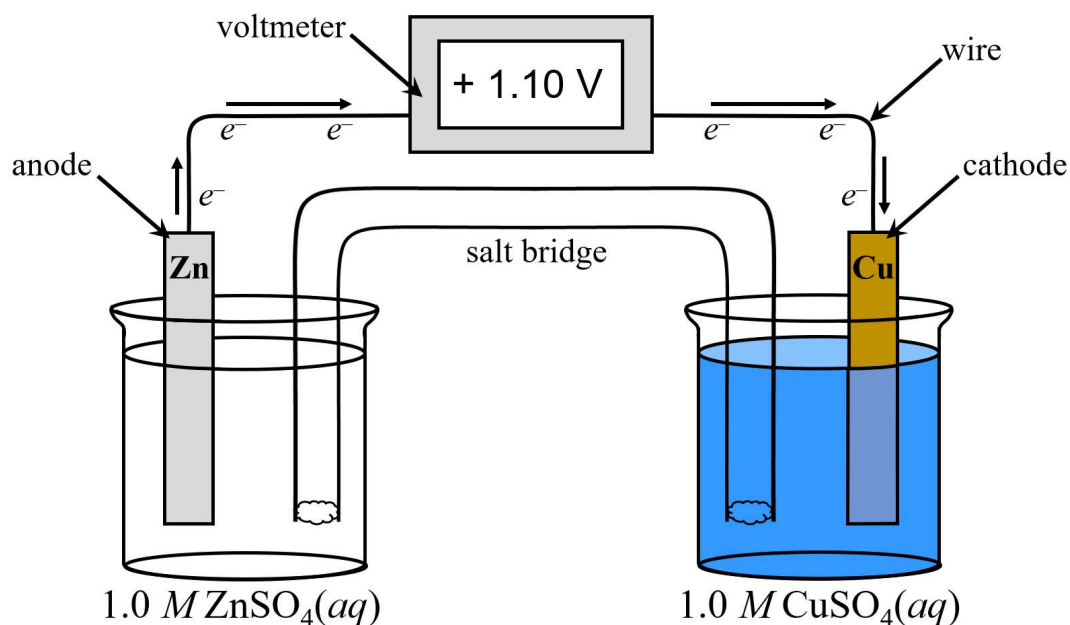


- (b) Write the net ionic equation for the reaction that you classified as thermodynamically favored in part (a).

1. (continued)

- (c) In the equation that you wrote in part (b), identify the species that is oxidized and the species that is reduced.

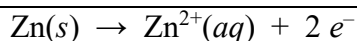
A galvanic cell (also known as a voltaic cell) can be constructed that is based on the thermodynamically favorable reaction from Question #1.



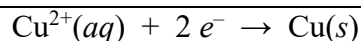
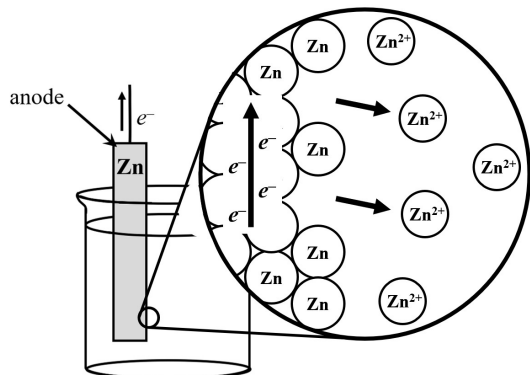
**On the AP Chemistry Exam, you CANNOT assume that the anode is always on the left side of the diagram. Pay attention to the specific information given in the problem.**

The features of this galvanic cell include the following,

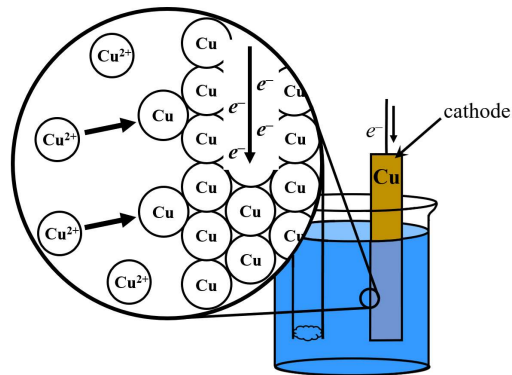
- Oxidation occurs at the anode:  $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$
- Reduction occurs at the cathode:  $\text{Cu}^{2+}(aq) + 2e^{-} \rightarrow \text{Cu}(s)$
- Electrons flow through the wire. Electrons travel from the anode (where oxidation occurs) toward the cathode (where reduction occurs.)
- As the reaction in this galvanic cell proceeds over time,
  - the mass of the Zn electrode (anode) decreases because atoms of  $\text{Zn}(s)$  are converted into  $\text{Zn}^{2+}(aq)$  ions that enter the solution.
  - the mass of the Cu electrode (cathode) increases because  $\text{Cu}^{2+}(aq)$  ions are converted into  $\text{Cu}(s)$  atoms that are deposited on the surface of the cathode.
- The salt bridge is an essential component of a galvanic cell.
  - It is often a tube filled with an aqueous solution of an electrolyte. This can be  $\text{KNO}_3(aq)$  or  $\text{Na}_2\text{SO}_4(aq)$  or any ionic compound that does not react with the reactants or the products.
  - If the salt bridge is removed, the voltage drops to zero.
  - The purpose of the salt bridge is to allow ions to flow into each half-cell container in order to balance the overall charge in each container.
  - Electrons do NOT flow through the salt bridge. Ions flow through the salt bridge.
  - Cations move toward the cathode, and anions move toward the anode.



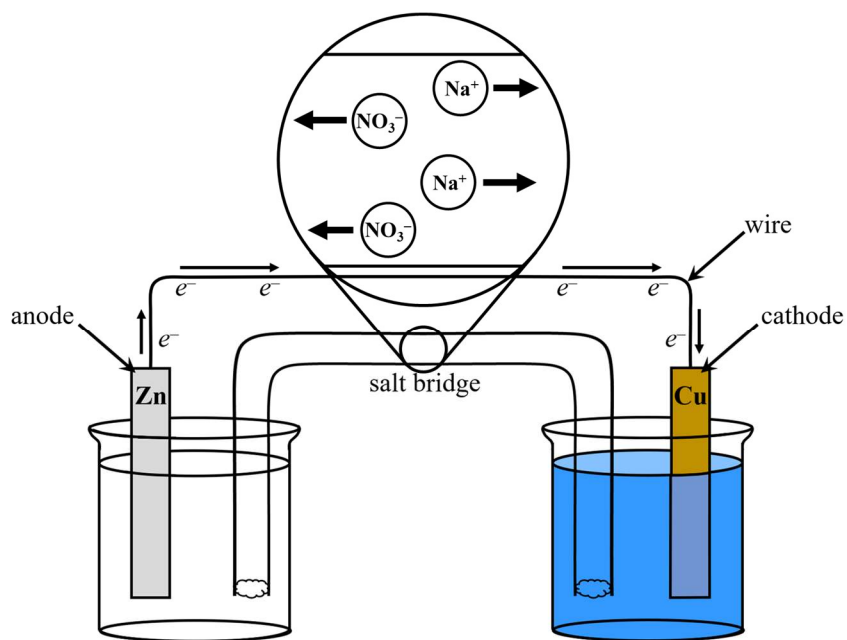
In the anode half-cell, Zn atoms are converted into  $\text{Zn}^{2+}$  ions, which dissolve and enter the solution. As the cell operates, the mass of the  $\text{Zn}(s)$  anode decreases. Electrons are released in this oxidation reaction and flow through the wire from the anode toward the cathode.

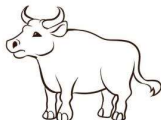



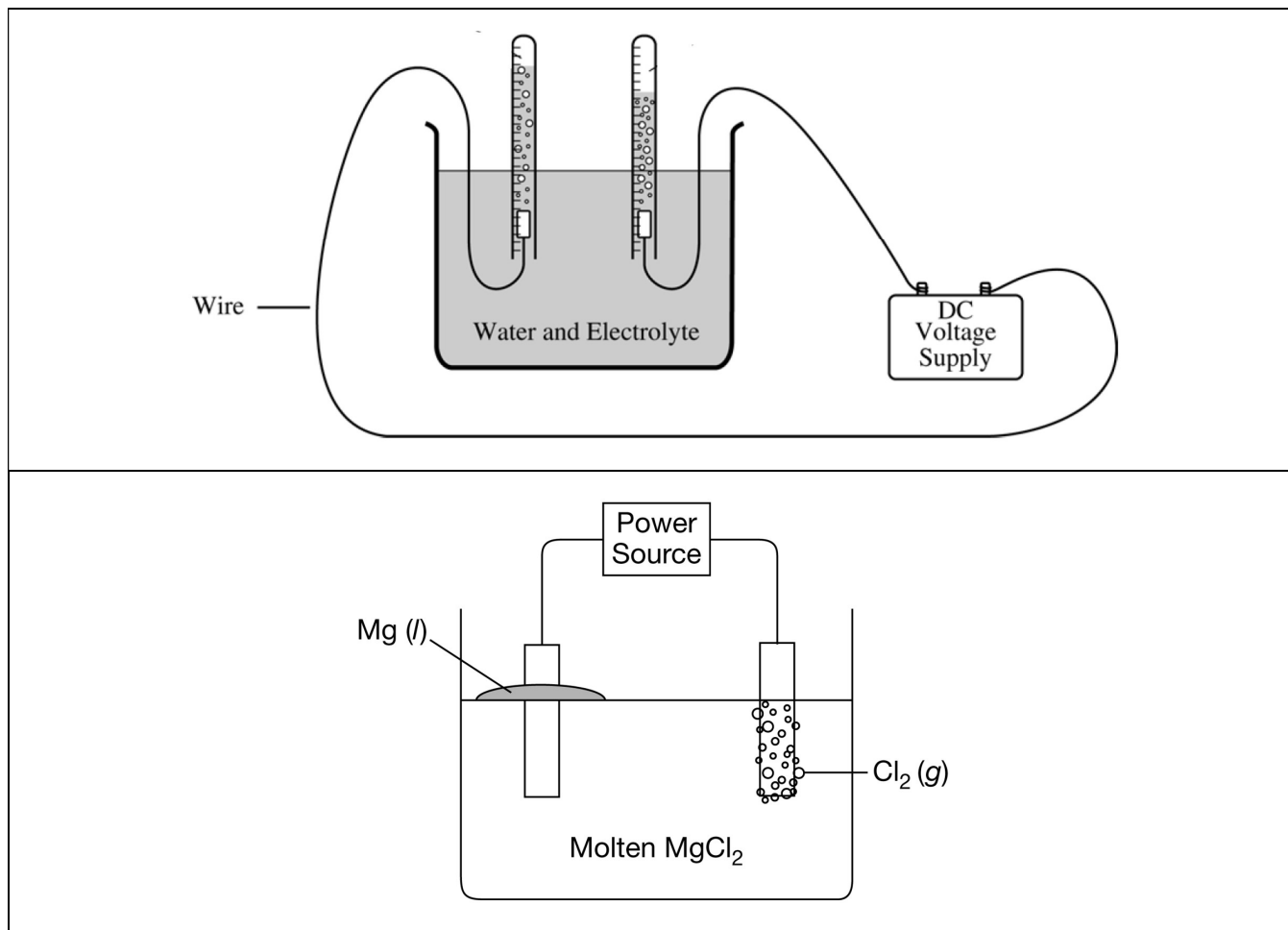
In the cathode half-cell,  $\text{Cu}^{2+}$  ions gain electrons that have traveled from the anode to the cathode. Aqueous  $\text{Cu}^{2+}$  ions are converted into Cu atoms, which are deposited on the cathode. As the cell operates, the mass of the  $\text{Cu}(s)$  cathode increases.



Electrons do NOT flow through the salt bridge.  
 Cations move toward the cathode, which is in the reduction half-cell.  
 Anions move toward the anode, which is in the oxidation half-cell.  
 The movement of ions in the salt bridge occurs in order to balance the overall charge in each half-cell container.

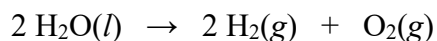


Oxidation occurs at the Anode	Reduction occurs at the Cathode
 AN OX	 RED CAT



2. Experimental setups for two different electrolytic cells are shown above.

- (a) Identify a specific item that is included in each setup that supports the fact that the reaction that occurs in the electrolytic cell is NOT thermodynamically favored. \_\_\_\_\_



- (b) Complete each sentence based on the redox equation shown above.

At the ( anode cathode ), \_\_\_\_\_ is oxidized from \_\_\_\_\_ to \_\_\_\_\_.

At the ( anode cathode ), \_\_\_\_\_ is reduced from \_\_\_\_\_ to \_\_\_\_\_.



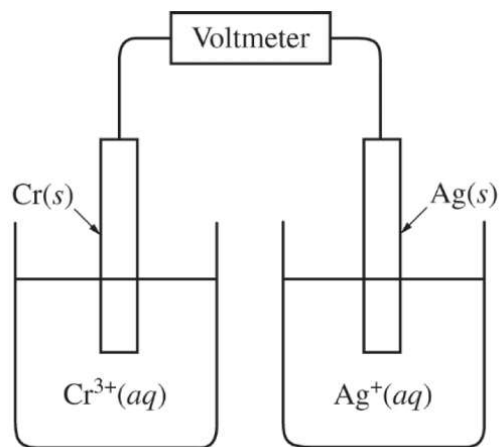
- (c) Complete each sentence based on the redox equation shown above.

At the ( anode cathode ), \_\_\_\_\_ is oxidized from \_\_\_\_\_ to \_\_\_\_\_.

At the ( anode cathode ), \_\_\_\_\_ is reduced from \_\_\_\_\_ to \_\_\_\_\_.

	Galvanic Cell (also known as a Voltaic Cell)	Electrolytic Cell
Thermodynamic Favorability	Favorable Reaction	Unfavorable Reaction
How is Electrical Energy Involved in this Reaction?	You can think of this as a battery, because this chemical reaction <u>produces</u> electrical energy.	Electrical energy from an external power source (e.g., a battery) is <u>required</u> in order for this chemical reaction to occur.
Change in Free Energy, $\Delta G^\circ$ (kJ/mol)	negative	positive
Cell Potential, $E^\circ$ (V)	positive	negative
Oxidation occurs at the...	Anode	Anode
Reduction occurs at the...	Cathode	Cathode
Direction of electron flow	Electrons travel through the wire, from the anode to the cathode	Electrons travel through the wire, from the anode to the power source to the cathode
Number of Containers	The anode half-cell and the cathode half-cell are in two separate containers	The anode and cathode are often in the same container.
Salt Bridge	required	not required

3. A student sets up a galvanic cell with a  $\text{Cr}(s)$  electrode immersed in a  $1.0\text{ M}$  solution of  $\text{Cr}^{3+}(aq)$  and a  $\text{Ag}(s)$  electrode immersed in a  $1.0\text{ M}$  solution of  $\text{Ag}^+(aq)$ , as shown in the diagram at right.



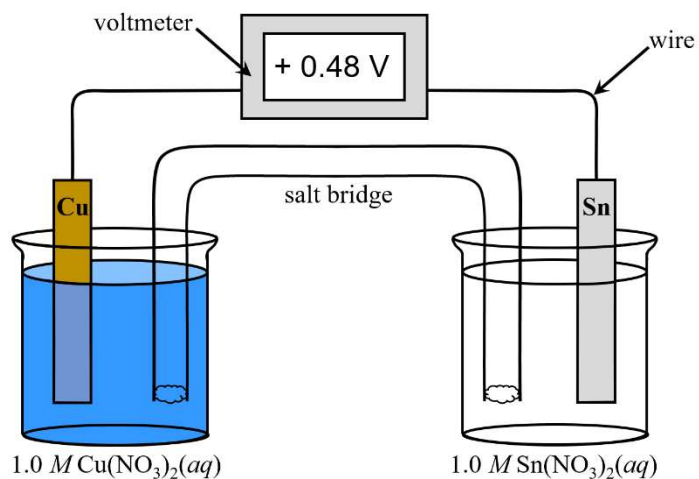
- (a) The student measures the voltage in the cell shown at right and discovers that it is zero. Identify the missing component of the cell.

- (b) What is the main purpose of the missing component that you chose in part (a)?

3. (continued)

- (c) The student adds the missing component to the cell. A voltmeter is used to measure the standard cell potential ( $E^\circ$ ), which is recorded as +1.54 V. As the cell operates, the mass of the Ag(s) electrode increases. Based on this information, write the balanced net ionic equation for the overall chemical reaction that occurs as the galvanic cell operates.

4. A student sets up a standard galvanic cell, with a Cu(s) electrode immersed in a solution of 1.0 M Cu(NO<sub>3</sub>)<sub>2</sub>(aq) and a Sn(s) electrode immersed in a solution of 1.0 M Sn(NO<sub>3</sub>)<sub>2</sub>(aq). As current flows through the cell, the student determines that the mass of the Cu(s) electrode increases and the mass of the Sn(s) electrode decreases.



- (a) Identify the electrode that represents the anode and the electrode that represents the cathode in this galvanic cell.

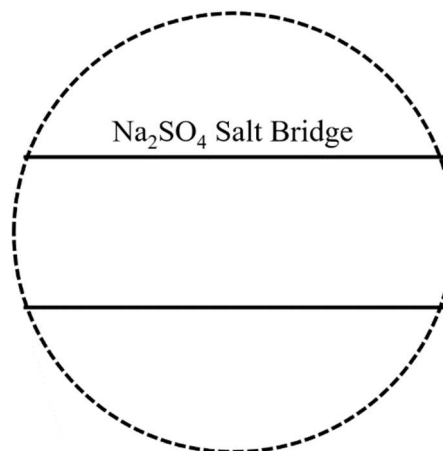
anode = \_\_\_\_\_ cathode = \_\_\_\_\_

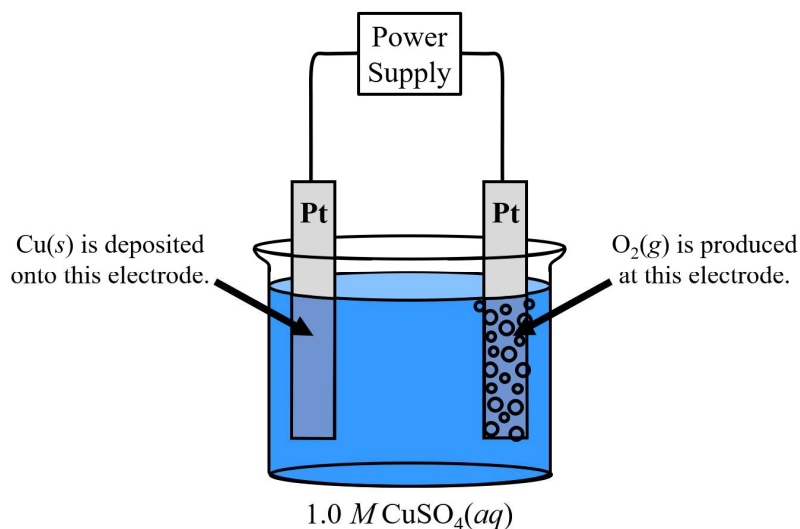
- (b) Write the net ionic equation for the half-reaction that occurs at each electrode.

Half-Reaction that Occurs at the Anode	Half-Reaction that Occurs at the Cathode

- (c) On the diagram above, draw an arrow to indicate the direction of electron flow in the wire as the galvanic cell operates.

- (d) A solution of sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>(aq), is used in the salt bridge. In the expanded view of the center portion of the salt bridge shown in the diagram at right, draw and label a particle view of what occurs in the salt bridge as the cell begins to operate. Omit solvent molecules and use arrows to show the direction of movement of the particles.





5. An external direct-current power supply is connected to two platinum electrodes immersed in a beaker containing  $1.0\text{ M CuSO}_4(aq)$  at  $25^\circ\text{C}$ , as shown in the diagram above. As the cell operates, copper metal is deposited onto one electrode, and  $\text{O}_2(g)$  is produced at the other electrode. Two reduction half-reactions are listed in the table below, along with the value of the standard reduction potential ( $E^\circ$ ) for each half-reaction.

Half-Reaction	$E^\circ$ (V)
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$	+1.23
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	+0.34

- (a) Is the overall chemical reaction that occurs in this electrochemical cell classified as thermodynamically favored or unfavored? Justify your answer.
- (b) The cell potential ( $E^\circ$ ) for the overall chemical reaction that occurs in this electrochemical cell should be ( positive negative ) because an external power source is required in order for the reaction to occur.
- (c) Write the net ionic equation for the half-reaction that occurs at each electrode.

Half-Reaction that Occurs at the Anode	Half-Reaction that Occurs at the Cathode

- (d) When combining two different half-reactions to produce the overall equation for a redox reaction, the total number of electrons gained should be equal to the total number of electrons lost. Use the information from the table above to write a balanced net ionic equation for the chemical reaction that occurs in this electrochemical cell.

5. (continued)

- (e) Calculate the value of the standard cell potential ( $E^\circ$ ), in volts, for the chemical reaction that occurs in this electrolytic cell. \_\_\_\_\_
- (f) On the diagram on the previous page, draw an arrow to indicate the direction of electron flow in the wire as the electrolytic cell operates.
- 

## 9.8 Cell Potential and Free Energy

Essential knowledge statements from the AP Chemistry CED:

- Electrochemistry encompasses the study of redox reactions that occur within electrochemical cells. The reactions are either thermodynamically favored (resulting in a positive voltage) or thermodynamically unfavored (resulting in a negative voltage and requiring an externally applied potential for the reaction to proceed).
  - The standard cell potential of electrochemical cells can be calculated by identifying the oxidation and reduction half-reactions and their respective standard reduction potentials.
  - $\Delta G^\circ$  (standard Gibbs free energy change) is proportional to the negative of the cell potential for the redox reaction from which it is constructed. Thus, a cell with a positive  $E^\circ$  involves a thermodynamically favored reaction, and a cell with a negative  $E^\circ$  involves a thermodynamically unfavored reaction.
    - $\Delta G^\circ = -nFE^\circ$
- 

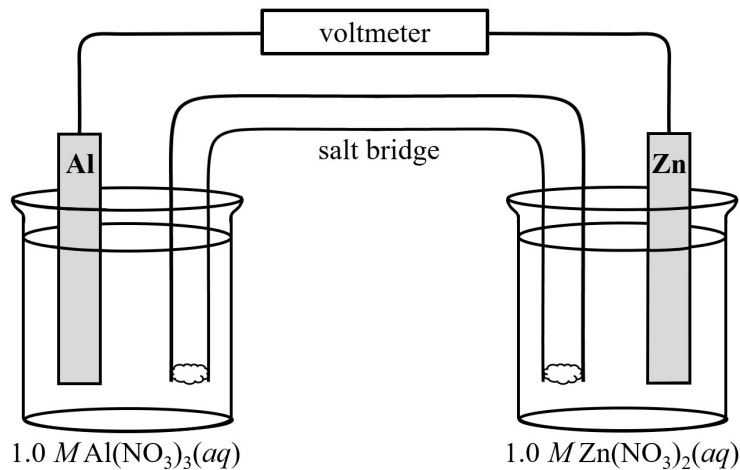
### Guidelines for Manipulating Half-Reactions

- The standard cell potential ( $E^\circ$ ) is positive for the reaction that occurs in a galvanic cell.
- The standard cell potential ( $E^\circ$ ) is negative for the reaction that occurs in an electrolytic cell.
- When combining two different half-reactions to produce the overall equation for a redox reaction, the total number of electrons gained should be equal to the total number of electrons lost.
- If a half-reaction is reversed, the sign of  $E^\circ$  is reversed.
- Multiplying a half-reaction by a constant N does NOT change the value of  $E^\circ$ .
- One volt (V) is equal to 1 joule per coulomb (J/C). The joule (J) is a unit of energy, and the coulomb (C) is a unit of electric charge. If a half-reaction is multiplied by a constant N, both the joules and the coulombs are each multiplied by N. Therefore the ratio of J/C remains the same, and value of the cell potential ( $E^\circ$ ), also known as the voltage, remains the same. This is the reason why the value of the cell potential is NOT multiplied by N when a half-reaction is multiplied by N.

### Guidelines for Calculations involving the Equation $\Delta G^\circ = -nFE^\circ$

- If the standard cell potential ( $E^\circ$ ) is positive, the standard free energy change ( $\Delta G^\circ$ ) is negative.
- If the standard cell potential ( $E^\circ$ ) is negative, the standard free energy change ( $\Delta G^\circ$ ) is positive.
- The variable  $n$  represents the total number of moles of electrons transferred in the overall balanced equation for the redox reaction.
- The Faraday constant is equal to 96,485 coulombs (C) per mole of electrons.
- 1 coulomb (C) multiplied by 1 volt (V) is equal to 1 joule (J).
- The units of  $\Delta G^\circ$  are usually reported in units of  $\text{kJ/mol}_{\text{rxn}}$ .





6. A student sets up a standard galvanic cell, with a  $\text{Al}(s)$  electrode immersed in  $1.0\text{ M Al(NO}_3)_3(aq)$  and a  $\text{Zn}(s)$  electrode immersed in  $1.0\text{ M Zn(NO}_3)_2(aq)$ . The standard reduction potential ( $E^\circ$ ) for each metal is listed in the table below.

Half-Reaction	$E^\circ$ (V)
$\text{Al}^{3+}(aq) + 3 e^- \rightarrow \text{Al}(s)$	-1.66
$\text{Zn}^{2+}(aq) + 2 e^- \rightarrow \text{Zn}(s)$	-0.76

- (a) Write the balanced net-ionic equation for the reaction that occurs as this galvanic cell operates.

- (b) Calculate the value of the standard cell potential ( $E^\circ$ ), in volts, for the chemical reaction that occurs in this galvanic cell. \_\_\_\_\_

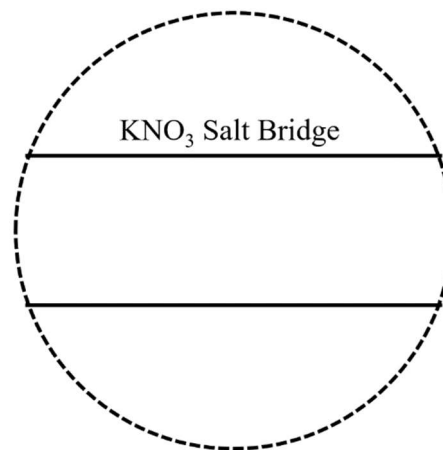
- (c) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , in units of  $\text{kJ/mol}_{rxn}$ , for the chemical reaction that occurs in this galvanic cell.

- (d) In this voltaic cell,  $\text{Al}(s)$  represents the ( anode cathode ). The mass of the  $\text{Al}(s)$  electrode will ( decrease increase ) as the cell operates.  $\text{Zn}(s)$  represents the ( anode cathode ). The mass of the  $\text{Zn}(s)$  electrode will ( decrease increase ) as the cell operates.

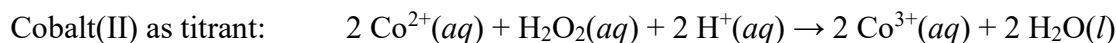
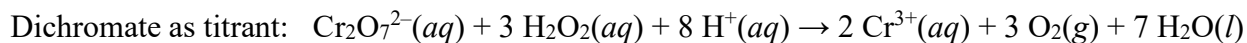
- (e) On the diagram above, draw an arrow to indicate the direction of electron flow in the wire as the galvanic cell operates.

6. (continued)

- (f) A solution of potassium nitrate,  $\text{KNO}_3(aq)$ , is used in the salt bridge. In the expanded view of the center portion of the salt bridge shown in the diagram at right, draw and label a particle view of what occurs in the salt bridge as the cell begins to operate. Omit solvent molecules and use arrows to show the direction of movement of the particles.



7. A student wants to determine the concentration of  $\text{H}_2\text{O}_2$  in a solution of  $\text{H}_2\text{O}_2(aq)$ . The student can use one of two titrants, either dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}(aq)$ , or cobalt(II) ion,  $\text{Co}^{2+}(aq)$ . The balanced chemical equations for the two titration reactions are shown below.



The half-reactions and the standard reduction potentials ( $E^\circ$ ) for the systems related to the titrations above are listed in the following table.

Half-Reaction	$E^\circ$ (V)
$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$	+1.84
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	+1.77
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	+1.33
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2\text{O}_2(aq)$	+0.70

- (a) Use the information in the table to calculate the following.



7. (continued)

(b) Based on the calculated values of  $E^\circ$ , the student must choose the titrant for which the titration reaction is thermodynamically favorable at standard conditions.

(i) Which titrant,  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$  or  $\text{Co}^{2+}(\text{aq})$ , should the student choose? Explain your reasoning.

(ii) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , in units of  $\text{kJ/mol}_{\text{rxn}}$ , for the reaction between the chosen titrant and  $\text{H}_2\text{O}_2(\text{aq})$ .

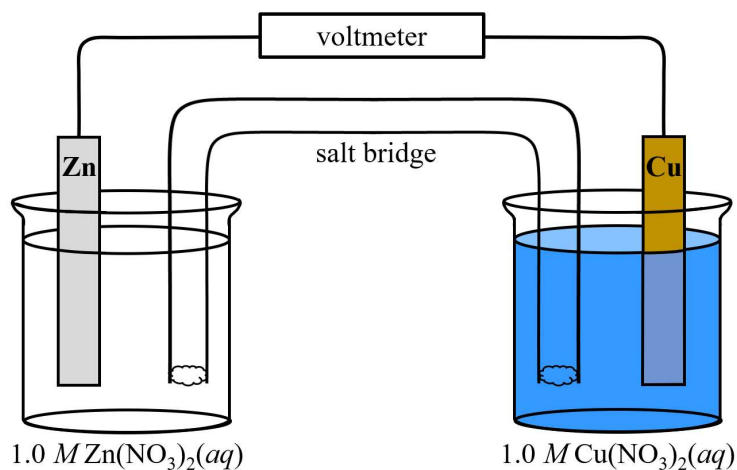
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## 9.9 Cell Potential Under Nonstandard Conditions

Essential knowledge statements from the AP Chemistry CED:

- In a real system under nonstandard conditions, the cell potential will vary depending on the concentrations of the active species. The cell potential is a driving force toward equilibrium; the farther the reaction is from equilibrium, the greater the magnitude of the cell potential.
- Equilibrium arguments such as Le Châtelier's principle do not apply to electrochemical systems, because the systems are not in equilibrium.
- The standard cell potential  $E^\circ$  corresponds to the standard conditions of  $Q = 1$ . As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential decreases, reaching zero at equilibrium (when  $Q = K$ ). Deviations from standard conditions that take the cell further from equilibrium than  $Q = 1$  will increase the magnitude of the cell potential relative to  $E^\circ$ . Deviations from standard conditions that take the cell closer to equilibrium than  $Q = 1$  will decrease the magnitude of the cell potential relative to  $E^\circ$ . In concentration cells, the direction of spontaneous electron flow can be determined by considering the direction needed to reach equilibrium.
- Algorithmic calculations using the Nernst equation are insufficient to demonstrate an understanding of electrochemical cells under nonstandard conditions. However, students should qualitatively understand the effects of concentration on cell potential and use conceptual reasoning, including the qualitative use of the Nernst equation to solve problems.
  - $E = E^\circ - (RT/nF) \ln Q$

	Standard Conditions	Nonstandard Conditions
Concentration of Aqueous Solutions	Aqueous solutions of reactant(s) and product(s) are equal to 1.0 <i>M</i> .	At least one of the aqueous solutions is NOT equal to 1.0 <i>M</i> .
Partial Pressure of Gases (if gases are present)	Partial pressures of gaseous reactant(s) and/or product(s) are equal to 1.0 atm.	At least one of the gaseous substances has a partial pressure that is NOT equal to 1.0 atm.
Temperature	Temperature is 298 K	Temperature is NOT 298 K
Reaction Quotient <i>Q</i>	<i>Q</i> is equal to 1.0	It is likely that <i>Q</i> is NOT equal to 1.0



8. A student sets up a standard galvanic cell at 298 K, with a Zn(*s*) electrode immersed in 1.0 *M* Zn(NO<sub>3</sub>)<sub>2</sub>(*aq*) and a Cu(*s*) electrode immersed in 1.0 *M* Cu(NO<sub>3</sub>)<sub>2</sub>(*aq*). The standard reduction potential (*E*<sup>°</sup>) for each metal is listed in the table below.

Half-Reaction	<i>E</i> <sup>°</sup> (V)
Zn <sup>2+</sup> ( <i>aq</i> ) + 2 <i>e</i> <sup>-</sup> → Zn( <i>s</i> )	-0.76
Cu <sup>2+</sup> ( <i>aq</i> ) + 2 <i>e</i> <sup>-</sup> → Cu( <i>s</i> )	+0.34

- (a) Write the balanced net-ionic equation for the reaction that occurs when this galvanic cell operates.

- (b) The value of the standard cell potential (*E*<sup>°</sup>) for this chemical reaction is \_\_\_\_\_ V.

8. (continued)

The expression for the reaction quotient ( $Q$ ) for this galvanic cell is written as follows:

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

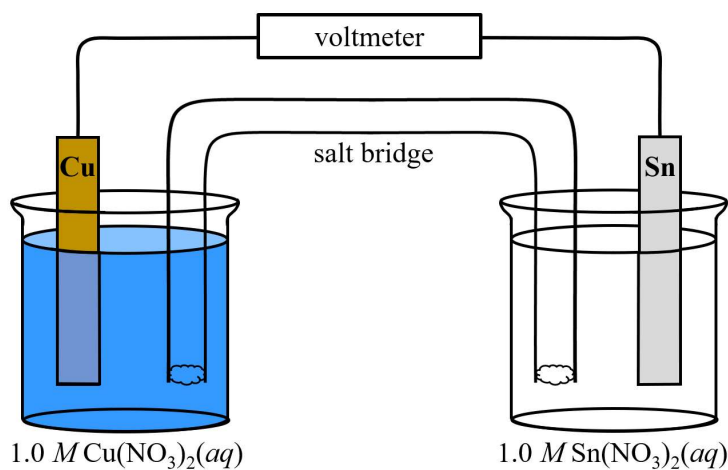
- (c) When this galvanic cell is set up at standard conditions,  $[\text{Zn}^{2+}] = [\text{Cu}^{2+}] = 1.0 \text{ M}$ , and the initial value of  $Q$  is equal to \_\_\_\_\_. As the cell operates over time, the value of  $[\text{Cu}^{2+}]$  ( decreases increases ), and the value of  $[\text{Zn}^{2+}]$  ( decreases increases ). As the cell runs, the value of  $Q$  gradually ( decreases increases ), and the value of the cell potential ( $E$ ) gradually ( decreases increases ). If this galvanic cell is run for a very long time, the value of the cell potential ( $E$ ) will eventually reach a value of \_\_\_\_\_. When this happens, we say that the galvanic cell has reached a state of equilibrium. At this point, that the cell is “dead,” and there is no longer a driving force for the reaction. The value of  $\Delta G$  for a galvanic cell that has reached equilibrium is equal to \_\_\_\_\_.
- (d) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , in units of  $\text{kJ/mol}_{\text{rxn}}$ , for the overall chemical reaction that occurs in this galvanic cell.
- (e) The answer to part (d) makes sense. Since the reaction that occurs in a galvanic cell ( is is not ) thermodynamically favored, the sign of  $\Delta G^\circ$  should be ( positive negative ).
- (f) Calculate the value of the equilibrium constant,  $K$ , for the overall chemical reaction that occurs in this galvanic cell.
- (g) The answer to part (f) makes sense. Since the reaction that occurs in a galvanic cell ( is is not ) thermodynamically favored, the value of  $K$  should be ( less greater ) than 1.

### Standard Conditions and Nonstandard Conditions for the Zn/Cu Galvanic Cell

Equation	$E^\circ$	$\Delta G^\circ$	$K$
$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$	+1.10 V	-212 kJ/mol	$1.5 \times 10^{37}$

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Farther Away From Equilibrium than Standard Conditions	Standard Conditions	Closer To Equilibrium than Standard Conditions	At Equilibrium The cell is "dead"
$Q < 1$	$Q = 1$	$Q > 1$	$Q = K = 1.5 \times 10^{37}$
$E > E^\circ$	$E = E^\circ$	$E < E^\circ$	$E = \text{zero}$
$[\text{Zn}^{2+}] < [\text{Cu}^{2+}]$ decreased [product] or increased [reactant] compared to standard conditions	$[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$ [product] = [reactant]	$[\text{Zn}^{2+}] > [\text{Cu}^{2+}]$ increased [product] or decreased [reactant] compared to standard conditions	$[\text{Zn}^{2+}] \gg [\text{Cu}^{2+}]$



9. A student sets up a standard galvanic cell using copper (Cu) and tin (Sn). The standard reduction potential ( $E^\circ$ ) for each metal is listed in the table below.

Half-Reaction	$E^\circ$ (V)
$\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu}(s)$	+0.34
$\text{Sn}^{2+}(aq) + 2 e^- \rightarrow \text{Sn}(s)$	-0.14

9. (continued)

- (a) Write the balanced net-ionic equation for the reaction that occurs when this galvanic cell operates.

- (b) Calculate the value of the standard cell potential ( $E^\circ$ ), in volts, for the chemical reaction that occurs in this galvanic cell. \_\_\_\_\_

In addition to the standard galvanic cell, the student also sets up three nonstandard galvanic cells. In each cell, the volumes of solutions used in each half-cell container are identical. The details of all four galvanic cells are summarized in the table below.

Cell	[Cu <sup>2+</sup> ]	[Sn <sup>2+</sup> ]	$Q$	Cell Potential, $E$ (V)		
#1	1.0 M	1.0 M	1.0	equal to 0.48		
#2	0.50 M	0.50 M		less than 0.48	equal to 0.48	greater than 0.48
#3	2.0 M	1.0 M		less than 0.48	equal to 0.48	greater than 0.48
#4	1.0 M	2.0 M		less than 0.48	equal to 0.48	greater than 0.48

- (c) Complete the missing information for galvanic cells #2, #3, and #4 in the table above. Your predictions about the value of  $E$  in the far right column of the table should be based on the qualitative use of the Nernst equation.

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Sn}^{2+}]}{[\text{Cu}^{2+}]}$$

- (d) Galvanic cell #1 and galvanic cell #2 can each be used to power an electronic device. Would galvanic cell #2 power the device for the same time, a longer time, or a shorter time as compared with galvanic cell #1? Justify your answer.
- (e) The student observes that increasing the size of the Sn(*s*) electrode that is used in cell #1 has no effect on the value of the cell potential ( $E$ ). Explain this observation.

9. (continued)

(f) A student sets up a standard galvanic cell using copper (Cu) and tin (Sn), and cell potential is recorded as 0.48 V. Then a small amount of NaOH(aq) is added to the beaker that contains 1.0 M Cu(NO<sub>3</sub>)<sub>2</sub>(aq). A solid precipitate of Cu(OH)<sub>2</sub>(s) forms in the solution. The precipitate settles at the bottom of the beaker.

(i) How does the formation of the Cu(OH)<sub>2</sub>(s) precipitate in this beaker affect the value of [Cu<sup>2+</sup>] in the solution? Justify your answer.

(ii) As a result of the formation of the Cu(OH)<sub>2</sub>(s) precipitate, the value of  $Q$  for this galvanic cell should become ( less greater ) than 1. The value of the cell potential ( $E$ ) for this galvanic cell should become ( less greater ) than 0.48 V.

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## 9.10 Electrolysis and Faraday's Law

Essential knowledge statement from the AP Chemistry CED:

- Faraday's laws can be used to determine the stoichiometry of the redox reaction occurring in an electrochemical cell with respect to the following:
  - Number of electrons transferred
  - Mass of material deposited on or removed from an electrode
  - Current
  - Time elapsed
  - Charge of ionic species
  - $I = q/t$

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### THERMODYNAMICS/ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

$q$  = heat

$m$  = mass

$c$  = specific heat capacity

$T$  = temperature

$S^\circ$  = standard entropy

$H^\circ$  = standard enthalpy

$G^\circ$  = standard Gibbs free energy

$n$  = number of moles

$E^\circ$  = standard reduction potential

$I$  = current (amperes)

$q$  = charge (coulombs)

$t$  = time (seconds)

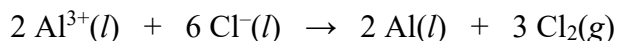
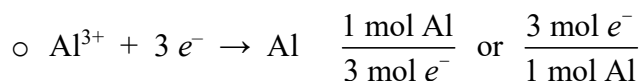
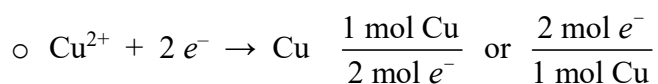
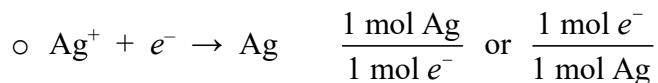
$Q$  = reaction quotient

Faraday's constant,  $F$  = 96,485 coulombs per mole of electrons

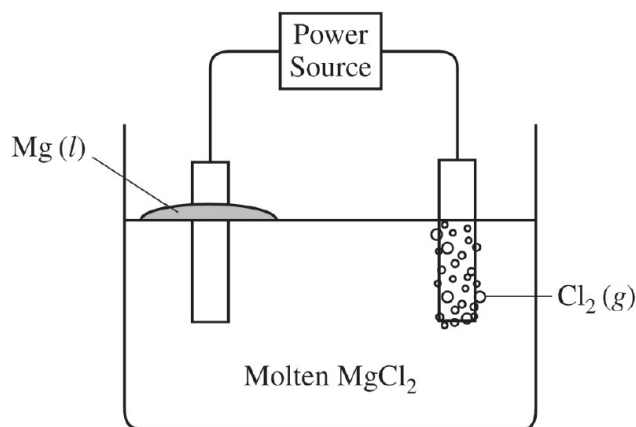
$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



- On the AP Chemistry Equations and Constants sheet,
  - $I$  = current (amperes)
  - $q$  = electric charge (coulombs)
  - $t$  = time (seconds)
- The units of electric current are amperes (A).
- 1 ampere (A) = 1 coulomb (C) per second (s), or  $1 \text{ A} = 1 \text{ C/s}$
- The Faraday constant ( $F$ ) gives the relationship between moles of electrons and charge.
  - 1 mole of electrons = 96,485 C
- The relationship between moles of electrons and moles of product formed in an electrolytic cell is related to the coefficients in the half-reaction. A few examples are shown below.



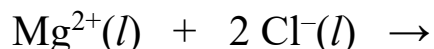
10. Electric current is passed through a solution of molten aluminum chloride,  $\text{AlCl}_3(l)$ . A steady electric current of 10.0 A passes through the cell. The products of the reaction are  $\text{Al}(l)$  and  $\text{Cl}_2(g)$  according to the equation shown above.
- (a) Calculate the mass, in grams, of  $\text{Al}(l)$  that is deposited on the electrode in this cell after a period of 585 seconds.
- (b) Calculate the time, in seconds, that is required for 0.175 g  $\text{Al}(l)$  to be deposited on the electrode in this cell.



Half-Reaction	$E^\circ$ (V)
$\text{Mg}^{2+} + 2 e^- \rightarrow \text{Mg}$	-2.37
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	+1.36

11. Molten  $\text{MgCl}_2$  can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. As this electrolytic cell operates,  $\text{Mg}(l)$  is formed at one electrode and  $\text{Cl}_2(g)$  is formed at the other electrode. A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table above.

(a) Write the products of the reaction that occurs when this electrolytic cell operates.



(b) On the diagram above, label each electrode as either the anode or the cathode.

(c) Write the net ionic equation for the half-reaction that occurs at each electrode.

Half-Reaction that Occurs at the Anode	Half-Reaction that Occurs at the Cathode

(d) On the diagram above, draw an arrow to indicate the direction of electron flow in the wire as the electrolytic cell operates.

(e) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(f) If the current in the cell is kept at a constant 5.00 amps, calculate the amount of time, in seconds, that is required to produce 2.00 g of  $\text{Mg}(l)$ .

12. A fuel cell is an electrochemical cell that converts the chemical energy stored in a fuel into electrical energy. A cell that uses  $\text{H}_2(\text{g})$  as the fuel can be constructed based on the half-reactions listed in the table below.

Half-Reaction	$E^\circ$ (V)
$2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 4 e^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.40
$2 \text{H}_2\text{O}(\text{l}) + 2 e^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83

- (a) Write the balanced equation for the overall reaction that occurs when this fuel cell operates.

- (b) Calculate the value of the standard cell potential ( $E^\circ$ ), in volts, for the chemical reaction that occurs in this fuel cell.

- (c) As the fuel cell operates for a period of 652 seconds, 1.83 g  $\text{H}_2(\text{g})$  is consumed. Calculate the average current, in units of amperes, that passes through the cell during this time period.