AP Chemistry Electrochemistry Test

Name __________ Key __________

1. Which of the following occurs in the above half reaction?
   (A) \( \text{AlF}_6^{3-} \) is reduced at the cathode.
   (B) \( \text{Al} \) is oxidized at the anode.
   (C) Aluminum is converted from the -3 oxidation state to the 0 oxidation state.
   (D) \( \text{F}^- \) acts as a reducing agent.
   (E) \( \text{F}^- \) is reduced at the cathode.

\[ +3 \quad \text{AlF}_6^{3-} + 3 \ e^- \rightarrow \text{Al} + 6 \text{F}^- \]

2. \( 6 \text{I}^- + 2 \text{MnO}_4^- + 4 \text{H}_2\text{O}(l) \rightarrow 3 \text{I}_2(s) + 2 \text{MnO}_2(s) + \text{OH}^- \)
   Which of the following statements regarding the reaction represented by the equation above is correct?
   (A) Iodide ion is oxidized by hydroxide ion.
   (B) \( \text{MnO}_4^- \) is oxidized by iodide ion.
   (C) The oxidation number of manganese changes from +7 to +2.
   (D) The oxidation number of manganese remains the same.
   (E) The oxidation number of iodine changes from -1 to 0.

\[ -1 \quad +7 \quad 0 \quad +4 \]

3. \( \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}^{0} \quad E^0 = -0.44 \text{ volt} \)
   \( \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}^{0} \quad E^0 = -0.23 \text{ volt} \)
   The standard reduction potentials for two half reactions are given above. What is the equilibrium constant for the reaction below?
   \( \text{Fe}^{0} + \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} + \text{Ni}^{0} \)

\[ \Delta G^0 = -\frac{2}{(2)(96,485)(0.21)} \]
\[ \ln K = \frac{+40,524}{(8.314)(298)} \]
\[ K = 16.4 \]
\[ K = 1.3 \times 10^7 \]

4. A steady current of 10 amperes is passed through an aluminum-production cell for 15 minutes. Which of the following is the correct expression for calculating the number of grams of aluminum produced? (1 faraday = 96,500 coulombs)

   (A) \( \frac{(10)(15)(96500)}{(27)(60)} \) g
   (B) \( \frac{(10)(15)(27)}{(60)(96,500)} \) g
   (C) \( \frac{(10)(15)(60)(27)}{(96,500)(3)} \) g
   (D) \( \frac{(96,500)(27)}{(10)(15)(60)(3)} \) g
   (E) \( \frac{(27)(3)}{(96,500)(10)(15)(60)} \) g

5. What is the maximum mass of copper that could be plated out by electrolyzing aqueous CuCl\(_2\) for 16.0 hours at a constant current of 3.00 amperes? (1 faraday = 96,500 coulombs)

   (A) 28 grams  (B) 57 grams  (C) 64 grams  (D) 114 grams  (E) 128 grams

\[ \frac{16.0 \text{ hr}}{1 \text{ hr}} \times \frac{1 \text{ mol CL}_2}{2 \text{ mole } 1 \text{ mol} \text{ Cu}} \times \frac{63.5 \text{ g Cu}}{1 \text{ mol CL}_2} \]
\[ = 56.8 \text{ g} \]
6. \[ \text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu(s)} \]

An electrolytic cell based on the reaction represented above was constructed from zinc and copper half-cells. The observed voltage was found to be 1.00 volt instead of the standard cell potential, \( E^0 \), of 1.10 volts. Which of the following could correctly account for this observation?

(A) The copper electrode was larger than the zinc electrode.
(B) The \( \text{Zn}^{2+} \) electrolyte was \( \text{Zn(NO}_3\text{)}_2 \), while the \( \text{Cu}^{2+} \) electrolyte was \( \text{CuSO}_4 \).
(C) The \( \text{Zn}^{2+} \) solution was more concentrated than the \( \text{Cu}^{2+} \) solution.
(D) The solutions in the half-cells had different volumes.
(E) The salt bridge contained \( \text{KCl} \) as the electrolyte.

\[ 0^+ + 1^+ + 5^+ + 2^+ + 2^+ + 1^+ \]

\[ \text{3 Cu(s)} + 8 \text{H}^+(aq) + 2 \text{NO}_3^-(aq) \rightarrow 3 \text{Cu}^{2+}(aq) + 2 \text{NO}_2(g) + 4 \text{H}_2\text{O(l)} \]

7. True statements about the reaction represented above include which of the following?

I. \( \text{Cu(s)} \) acts as an oxidizing agent.
II. The oxidation state of nitrogen changes from +5 to +2.
III. Hydrogen ions are oxidized to form \( \text{H}_2\text{O(l)} \).

(A) I only (B) II only (C) III only (D) I and II (E) II and III

8. If a copper sample containing some zinc impurity is to be purified by electrolysis, the anode and the cathode must be which of the following?

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Pure copper</td>
<td>Pure zinc</td>
</tr>
<tr>
<td>(B) Pure zinc</td>
<td>Pure copper</td>
</tr>
<tr>
<td>(C) Pure copper</td>
<td>Impure copper sample</td>
</tr>
<tr>
<td>(D) Impure copper sample</td>
<td>Pure copper</td>
</tr>
<tr>
<td>(E) Impure copper sample</td>
<td>Pure zinc</td>
</tr>
</tbody>
</table>

9. If 0.060 faraday is passed through an electrolytic cell containing a solution of \( \text{In}^{3+} \) ions, the maximum number of moles of \( \text{In} \) that could be deposited at the cathode is

(A) 0.010 mole  (B) 0.030 mole  (C) 0.18 mole  (D) 0.020 mole  (E) 0.060 mole

\[
\frac{1 \text{ F is charge on 1 mole of} \ e^-}{3 \text{ mole} e^-} = \frac{0.06 F}{3} = 0.020 \text{ In}
\]

10. What element is utilized as a coating to protect Fe from corrosion

(A) \( \text{Pb} \)  (B) \( \text{Ca} \)  (C) \( \text{Zn} \)  (D) \( \text{As} \)  (E) \( \text{Na} \)
11. \[ \text{Cu}_{(s)} + 2 \text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2 \text{Ag}_{(s)} \]

If the equilibrium constant for the reaction above is \(3.7 \times 10^{15}\), which of the following correctly describes the standard voltage, \(E^*\), and the standard free energy change, \(\Delta G^*\), for this reaction?

(A) \(E^*\) is positive and \(\Delta G^*\) is negative.

(B) \(E^*\) is negative and \(\Delta G^*\) is positive.

(C) \(E^*\) and \(\Delta G^*\) are both positive.

(D) \(E^*\) and \(\Delta G^*\) are both negative.

(E) \(E^*\) and \(\Delta G^*\) are both zero

Questions 12–15

The spontaneous reaction occurring in the cell above is \(2 \text{Ag}^+ + \text{Cd}_{(s)} \rightarrow 2 \text{Ag}_{(s)} + \text{Cd}^{2+}\)

(A) Voltage increases.

(B) Voltage decreases.

(C) Voltage becomes zero and remains at zero.

(D) No change in voltage occurs.

(E) Direction of voltage change cannot be predicted without additional information.

Which of the above occurs for each of the following circumstances?

12. A 50-milliliter sample of a 2-molar \(\text{Cd(NO}_3\text{)}_2\) solution is added to the left beaker.

13. The silver electrode is made larger.

14. The salt bridge is replaced by a platinum wire.

15. Current is allowed to flow for 5 minutes.
AP Chemistry
Free-Response Scoring Guidelines

Question 5

Answer the following questions relating to the galvanic cell shown in the diagram above.

(a) Write the balanced equation for the overall cell reaction.

\[ 2 \text{Ag}^+(aq) + \text{Co}(s) \rightarrow 2 \text{Ag}(s) + \text{Co}^{2+}(aq) \]

One point is earned for the correct equation.

(b) Calculate the value of \(E^\circ\) for the cell.

\[ E^\circ_{cell} = 0.80 - (-0.28) = 1.08 \text{ V} \]

One point is earned for the correct value of \(E^\circ_{cell}\).

(c) Is the value of \(\Delta G^\circ\) for the overall cell reaction positive, negative, or 0? Justify your answer.

- The value of \(\Delta G^\circ\) for the overall reaction must be negative because the cell reaction occurs (is spontaneous) as the cell operates.

   OR

- Since \(E^\circ_{cell}\) is positive and \(\Delta G^\circ = -nFE^\circ\), the value of \(\Delta G^\circ\) must be negative.

   One point is earned for the correct answer, including a valid justification.
(d) Consider the cell as it is operating.

(i) Does \( E_{\text{cell}} \) increase, decrease, or remain the same? Explain.

As the cell operates, the concentration of \( \text{Ag}^+ \) decreases and the concentration of \( \text{Co}^{2+} \) increases \( \Rightarrow \) the ratio \( Q = \frac{[\text{Co}^{2+}]}{[\text{Ag}^+]^2} \) increases \( \Rightarrow \) \( \ln Q \) increases \( \Rightarrow \)

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q \quad \text{becomes smaller (decreases)}.
\]

One point is earned for the correct answer, including a valid justification.

(ii) Does \( \Delta G \) of the overall cell reaction increase, decrease, or remain the same? Explain.

The value of \( \Delta G \) for the system increases (becomes less negative) as the cell operates and the system approaches equilibrium (when \( \Delta G = 0 \)).

One point is earned for the correct answer, including a valid justification.

(iii) What would happen if the \( \text{NaNO}_3 \) solution in the salt bridge was replaced with distilled water? Explain.

The cell would not operate. The voltage of the cell is too small to overcome the electrical resistance of distilled water, which is a poor conductor due to its very low concentration of ions (about \( 10^{-7} \text{ M H}^+(\text{aq}) \) and \( 10^{-7} \text{ M OH}^-(\text{aq}) \)) that could "carry" the current from one cell to the other.

One point is earned for the correct answer, including a valid justification.

(e) After a certain amount of time, the mass of the \( \text{Ag} \) electrode changes by \( x \) grams. Given that the molar mass of \( \text{Ag} \) is \( 108 \text{ g mol}^{-1} \) and the molar mass of \( \text{Co} \) is \( 59 \text{ g mol}^{-1} \), write the expression for the change in the mass of the \( \text{Co} \) electrode in terms of \( x \).

\[
\Delta \text{ mol Ag} = \Delta \text{ mass Ag} \times \frac{1 \text{ mol Ag}}{108 \text{ g Ag}} = x \times \frac{1}{108} = \frac{x}{108}
\]

\[
\Delta \text{ mol Co} = -\Delta \text{ mol Ag} \times \frac{1 \text{ mol Co}}{2 \text{ mol Ag}} = -\frac{x}{108} \times \frac{1}{2} = -\frac{x}{216}
\]

\[
\Delta \text{ mass Co} = \Delta \text{ mol Co} \times \frac{59 \text{ g Co}}{1 \text{ mol Co}} = -\frac{x}{216} \times 59 = -\frac{59x}{216}
\]

One point is earned for using the correct mole ratio of \( \text{Co} \) to \( \text{Ag} \).

One point is earned for the correct answer (negative sign is not required).
In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

Observation 1: \( \text{Pb}^{2+}(aq) + X^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + X(s) \)
Observation 2: \( Q(s) + X^{2+}(aq) \rightarrow \) no reaction
Observation 3: \( \text{Pb}^2+(s) + Q^2+(aq) \rightarrow \text{Pb}^{2+}(aq) + Q(s) \)

(a) On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to most reactive on the lines provided below.

\[
\begin{array}{ccc}
Q & , & X & , & \text{Pb} \\
\text{least reactive metal} & & & & \text{most reactive metal}
\end{array}
\]

\[
\begin{array}{|c|c|}
\hline
Q, X, Pb & 2 \text{ points are earned for the correctly ordered relationship.} \\
\hline
\end{array}
\]

(1 point earned for Q, Pb, X or X, Q, Pb)
The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of 1.0 \( M \) Pb(NO\(_3\))\(_2\)(aq) and an electrode made of metal X immersed in 100. mL of 1.0 \( M \) X(NO\(_3\))\(_2\)(aq). A salt bridge containing saturated aqueous KNO\(_3\) connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.

(b) Write the equation for the half-reaction that occurs at the anode.

\[
Pb(s) \rightarrow Pb^{2+}(aq) + 2 \text{e}^- \quad \text{1 point is earned for the correct equation.}
\]

(c) The value of the standard potential for the cell, \( E^o \), is 0.47 V.

(i) Determine the standard reduction potential for the half-reaction that occurs at the cathode.

\[
E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}}
\]

\[
E^o_{\text{cathode}} = E^o_{\text{cell}} + E^o_{\text{anode}}
\]

\[
E^o_{\text{cathode}} = 0.47 + (-0.13) = 0.34 \text{ V}
\]

1 point is earned for the calculated reduction potential with mathematical justification.

\[
0.47 = x + 0.13
\]
(ii) Determine the identity of metal X.

| The metal is copper.            | 1 point is earned for identification of the metal. |

(d) Describe what happens to the mass of each electrode as the cell operates.

| The mass of the Pb electrode decreases and the mass of the Cu electrode increases. | 1 point is earned for both descriptions. |

(e) During a laboratory session, students set up the electrochemical cell shown above. For each of the following three scenarios, choose the correct value of the cell voltage and justify your choice.

(i) A student bumps the cell setup, resulting in the salt bridge losing contact with the solution in the cathode compartment. Is V equal to 0.47 or is V equal to 0? Justify your choice.

$$V = 0 \text{ V. The transfer of ions through the salt bridge will stop. A charge imbalance between the half-cells will prevent electrons from flowing through the wire.}$$  

1 point is earned for the correct choice with an appropriate explanation.

(ii) A student spills a small amount of 0.5 M Na₂SO₄(aq) into the compartment with the Pb electrode, resulting in the formation of a precipitate. Is V less than 0.47 or is V greater than 0.47? Justify your choice.

$$V > 0.47 \text{ V. The sulfate ion will react with the Pb}^{2+} \text{ ion to form a precipitate. This results in a thermodynamically favored anode half-cell reaction and hence a larger potential difference. The choice may also be justified using the Nernst equation.}$$  

$$E_{cell} = E_{cell}^o - \left( \frac{RT}{nF} \right) \ln \left( \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]} \right)$$  

Decreasing the [Pb²⁺] will increase the cell voltage.

1 point is earned for the correct choice with an appropriate explanation.

(iii) After the laboratory session is over, a student leaves the switch closed. The next day, the student opens the switch and reads the voltmeter. Is V less than 0.47 or is V equal to 0.47? Justify your choice.

$$V < 0.47 \text{ V. Over time, [Pb}^{2+}] \text{ increases and [Cu}^{2+}] \text{ decreases, making both half-cell reactions less thermodynamically favorable. The choice may also be justified using the Nernst equation. Increasing [Pb}^{2+}] \text{ and decreasing [Cu}^{2+}] \text{ decreases the cell voltage. The choice may also be justified by stating that the voltage is zero as a result of the establishment of equilibrium.}$$

$$\frac{q}{1} \rightarrow \ln q \text{ is positive}$$

1 point is earned for the correct choice with an appropriate explanation.
An external direct-current power supply is connected to two platinum electrodes immersed in a beaker containing 1.0 M CuSO₄(aq) at 25°C, as shown in the diagram above. As the cell operates, copper metal is deposited onto one electrode and O₂(g) is produced at the other electrode. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>E°(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂(g) + 4 H⁺(aq) + 4 e⁻ → 2 H₂O(l)</td>
<td>+1.23</td>
</tr>
<tr>
<td>Cu²⁺(aq) + 2 e⁻ → Cu(s)</td>
<td>+0.34</td>
</tr>
</tbody>
</table>

(a) On the diagram, indicate the direction of electron flow in the wire.

| The electron flow in the wire is from the right toward the left (counterclockwise). | One point is earned for the correct direction. |

(b) Write a balanced net ionic equation for the electrolysis reaction that occurs in the cell.

2 H₂O(l) + 2 Cu²⁺(aq) → 4 H⁺(aq) + 2 Cu(s) + O₂(g)

| One point is earned for all three products. |
| One point is earned for balancing the equation. |

(c) Predict the algebraic sign of ΔG° for the reaction. Justify your prediction.

| The sign of ΔG° would be positive because the reaction is NOT spontaneous. | One point is earned for indicating that ΔG° is greater than zero and supplying a correct explanation. |
(d) Calculate the value of $\Delta G^\circ$ for the reaction.

| $E^\circ = -1.23 \text{ V} + 0.34 \text{ V} = -0.89 \text{ V} = -0.89 \text{ J C}^{-1}$ | One point is earned for calculating $E^\circ$. |
| $\Delta G^\circ = -n \beta E^\circ = -4 (96,500 \text{ C mol}^{-1})(-0.89 \text{ J C}^{-1})$ | One point is earned for calculating $\Delta G^\circ$ (consistent with the calculated $E^\circ$). |
| $= +340,000 \text{ J mol}^{-1} = +340 \text{ kJ mol}^{-1}$ | |

An electric current of 1.50 amps passes through the cell for 40.0 minutes.

(e) Calculate the mass, in grams, of the Cu(s) that is deposited on the electrode.

| $q = (1.50 \text{ C s}^{-1})(40.0 \text{ min}) \times \frac{60 \text{ s}}{1 \text{ minute}} = 3,600 \text{ C}$ | One point is earned for calculating $q$. |
| mass Cu = (3,600 C) $\times \frac{1 \text{ mol} e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}}$ | One point is earned for calculating the mass of copper deposited. |
| = 1.19 g Cu | OR |
| Two points are earned for calculating the mass of copper in one step. | |

(f) Calculate the dry volume, in liters measured at 25°C and 1.16 atm, of the O$_2$(g) that is produced.

| $n_{O_2} = (1.19 \text{ g Cu}) \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol Cu}} = 0.00936 \text{ mol O}_2$ | One point is earned for calculating the number of moles of O$_2$. |
| $V = \frac{nRT}{P} = \frac{(0.00936 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.16 \text{ atm}}$ | One point is earned for calculating $V$ (consistent with previous calculations). |
| = 0.197 L | |
Overall reaction: \( \text{Pb}(s) + \text{PbO}_2(s) + 2 \text{H}^+(aq) + 2 \text{HSO}_4^-(aq) \rightarrow 2 \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l) \)

Cathode half-cell reaction: \( \text{PbO}_2(s) + 3 \text{H}^+(aq) + \text{HSO}_4^-(aq) + 2 \text{e}^- \rightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l) \)

The equations above represent reactions associated with the operation of a lead storage battery. The first is the overall reaction that occurs as the battery produces an electrical current, and the second is the half-reaction that occurs at the cathode.

(a) Determine the oxidation number of sulfur in the overall reaction.

\[ +6 \]
1 point is earned for the correct answer.

(b) Write the equation for the half-reaction that occurs at the anode as the battery operates.

\[ \text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2 \text{e}^- \]
1 point is earned for a correct equation.

After the battery has operated for some time, it can be recharged by applying a current to reverse the overall reaction.

(c) Calculate the time, in seconds, needed to regenerate 100. g of \( \text{Pb}(s) \) in the battery by applying a current of 5.00 amp.

\[
\begin{align*}
100. \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g}} &= 0.483 \text{ mol Pb} \\
0.483 \text{ mol Pb} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Pb}} &= 0.966 \text{ mol } e^- \\
0.966 \text{ mol } e^- \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} &= 93,200 \text{ C} \\
I = \frac{q}{t} \quad \Rightarrow \quad t &= \frac{q}{I} \\
93,200 \text{ C} \times \frac{1 \text{ amp}}{1 \text{ C/s}} &= 18,600 \text{ s}
\end{align*}
\]

1 point is earned for the correct number of moles of electrons (may be implicit).

1 point is earned for the correct time based on the moles of electrons.