AP® CHEMISTRY
2013 SCORING GUIDELINES

Question 2

Answer the following questions involving the stoichiometry and thermodynamics of reactions containing aluminum species.

$$2\ Al_2O_3(l) + 3\ C(s) \rightarrow 4\ Al(l) + 3\ CO_2(g)$$

An electrolytic cell produces 235 g of Al(l) according to the equation above.

(a) Calculate the number of moles of electrons that must be transferred in the cell to produce the 235 g of Al(l).

$235\text{ g Al} \times \dfrac{1\text{ mol Al}}{26.98\text{ g Al}} = 8.71\text{ mol Al}$	1 point is earned for the number of moles of Al.
$Al^{3+} + 3\,e^- \rightarrow Al$, therefore, 3 mol e^- transferred per mol Al $8.71\text{ mol Al} \times \dfrac{3\text{ mol }e^-}{1\text{ mol Al}} = 26.1\text{ mol }e^-$	1 point is earned for correct stoichiometry and the number of moles of electrons.

(b) A steady current of 152 amp was used during the process. Determine the amount of time, in seconds, that was needed to produce the Al(l).

charge $=$ moles $e^- \times$ Faraday's constant $= 26.1\text{ mol }e^- \times \dfrac{9.65 \times 10^4\text{ C}}{1\text{ mol }e^-} = 2.52 \times 10^6\text{ C}$	1 point is earned for the correct amount of charge transferred.
$I = \dfrac{q}{t}$ $t = \dfrac{q}{I} = \dfrac{2.52 \times 10^6\text{ C}}{152\text{ C/s}} = 1.66 \times 10^4\text{ s}$	1 point is earned for the correct time.

(c) Calculate the volume of $CO_2(g)$, measured at 301 K and 0.952 atm, that is produced in the process.

$\text{mol } CO_2 = 8.71\text{ mol Al} \times \dfrac{3\text{ mol } CO_2}{4\text{ mol Al}} = 6.53\text{ mol } CO_2$	1 point is earned for the number of moles of CO_2.
$PV = nRT$ $V = \dfrac{nRT}{P} = \dfrac{(6.53\text{ mol})\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(301\text{ K})}{0.952\text{ atm}} = 1.70 \times 10^2\text{ L } CO_2$	1 point is earned for the volume of CO_2.

Question 2 (continued)

(d) For the electrolytic cell to operate, the Al_2O_3 must be in the liquid state rather than in the solid state. Explain.

Al_2O_3 is an ionic compound; in the solid state it will not conduct electricity. In order for the cell to operate, Al_2O_3 must be in the liquid state so that the ions are mobile and able to move to the electrodes to react (and/or complete the circuit).	1 point is earned for a correct explanation.

When Al(*s*) is placed in a concentrated solution of KOH at 25°C, the reaction represented below occurs.

$$2\ Al(s) + 2\ OH^-(aq) + 6\ H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3\ H_2(g)$$

Half-reaction	$E°$ (V)
$[Al(OH)_4]^-(aq) + 3\ e^- \rightarrow Al(s) + 4\ OH^-(aq)$	–2.35
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	–0.83

(e) Using the table of standard reduction potentials shown above, calculate the following.

(i) $E°$, in volts, for the formation of $[Al(OH)_4]^-(aq)$ and $H_2(g)$ at 25°C

$E^\circ = E^\circ_{cathode} - E^\circ_{anode} = -0.83\text{ V} - (-2.35\text{ V}) = 1.52\text{ V}$	1 point is earned for the correct value of $E°$.

(ii) $\Delta G°$, in kJ/mol_{rxn}, for the formation of $[Al(OH)_4]^-(aq)$ and $H_2(g)$ at 25°C

$\Delta G^\circ = -nFE^\circ = -(6)(9.65 \times 10^4\text{ C})(1.52\text{ V})$ $= -8.80 \times 10^5\text{ J/mol}_{rxn} = -8.80 \times 10^2\text{ kJ/mol}_{rxn}$ (or $-880.$ kJ/mol_{rxn})	1 point is earned for $n = 6$. 1 point is earned for the correct value of $\Delta G°$.

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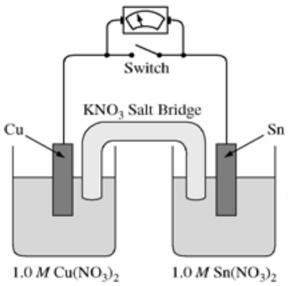
Question 3
(10 points)



A student is given a standard galvanic cell, represented above, that has a Cu electrode and a Sn electrode. As current flows through the cell, the student determines that the Cu electrode increases in mass and the Sn electrode decreases in mass.

(a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

Since the Sn electrode is losing mass, Sn atoms must be forming $Sn^{2+}(aq)$. This process is oxidation. OR because the cell operates, $E°$ must be positive and, based on the $E°$ values from the table, it must be Sn that is oxidized.	1 point is earned for the correct answer with justification.

(b) As the mass of the Sn electrode decreases, where does the mass go?

The atoms on the Sn electrode are going into the solution as Sn^{2+} ions.	1 point is earned for the correct answer.

(c) In the expanded view of the center portion of the salt bridge shown in the diagram below, 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 movement of particles.

The response should show at least one K^+ ion moving toward the Cu compartment on the left and at least one NO_3^- ion moving in the opposite direction.	1 point is earned for correct representation of both K^+ and NO_3^- ions. (Including free electrons loses this point.) 1 point is earned for correctly indicating the direction of movement of both ions.

Question 3 (continued)

(d) A nonstandard cell is made by replacing the 1.0 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$ in the standard cell with 0.50 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$. The volumes of solutions in the nonstandard cell are identical to those in the standard cell.

(i) Is the cell potential of the nonstandard cell greater than, less than, or equal to the cell potential of the standard cell? Justify your answer.

It is the same. In the cell reaction $Q = \frac{[Sn^{2+}]}{[Cu^{2+}]}$, and the concentrations of Sn^{2+} and Cu^{2+} are equal to each other in both cases.	1 point is earned for the correct answer with justification.

(ii) Both the standard and nonstandard cells can be used to power an electronic device. Would the nonstandard cell power the device for the same time, a longer time, or a shorter time as compared with the standard cell? Justify your answer.

The nonstandard cell would power the device for a shorter time because the supply of Cu^{2+} ions will be exhausted more quickly. OR The nonstandard cell would power the device for a shorter time because the reaction will reach $E = 0$ more quickly.	1 point is earned for the correct answer with justification.

(e) In another experiment, the student places a new Sn electrode into a fresh solution of 1.0 *M* $Cu(NO_3)_2$.

Half-Reaction	$E°$ (V)
$Cu^{+} + e^{-} \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$	0.34
$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+}$	0.15
$Sn^{2+} + 2e^{-} \rightarrow Sn(s)$	–0.14

(i) Using information from the table above, write a net-ionic equation for the reaction between the Sn electrode and the $Cu(NO_3)_2$ solution that would be thermodynamically favorable. Justify that the reaction is thermodynamically favorable.

Question 3 (continued)

$Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$	1 point is earned for the correct net-ionic equation.
$E°$ is positive (0.34 V + 0.14 V = 0.48 V), therefore the reaction is thermodynamically favorable. OR The cell observations from earlier parts of the question are evidence that the Sn is oxidized and Cu is reduced, therefore $E°$ must be positive.	1 point is earned for a correct justification (unit not needed in calculation).

(ii) Calculate the value of $\Delta G°$ for the reaction. Include units with your answer.

$\Delta G° = -nFE°$ $\Delta G° = -\frac{2 \text{ mol } e^-}{\text{mol}_{rxn}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{0.48 \text{ J}}{\text{C}} = -93{,}000 \text{ J/mol}_{rxn} = -93 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct number of electrons. 1 point is earned for the correct answer with unit.

Question 1

Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	E at pH 11 and 298 K (V)
$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$	+0.34
$ZnO(s) + H_2O(l) + 2\ e^- \rightarrow Zn(s) + 2\ OH^-(aq)$	−1.31
$Na_2O(s) + H_2O(l) + 2\ e^- \rightarrow 2\ Na(s) + 2\ OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\ e^- \rightarrow Ca(s) + 2\ OH^-(aq)$	−2.78

(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

$E_{cell} = 0.34\ V - (-1.31\ V) = 1.65\ V$	1 point is earned for the correct cell potential.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(The arrow should point to the left.)	1 point is earned for indicating the movement of OH^- ions from right to left in the cell.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

The mass increases.	1 point is earned for indicating an increase in cell mass.

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

Oxygen gas from the air reacts with $Zn(s)$ in the cell, producing $ZnO(s)$, which has more mass than the original $Zn(s)$.	1 point is earned for the justification.

Question 1 (continued)

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

The cell potential will be lower.	1 point is earned for indicating a lower cell potential.

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

$O_2(g)$, a reactant in the cell reaction, will be at a lower partial pressure at the higher elevation; thus the reaction has a greater value of Q (closer to K). Deviations in partial pressure that take the cell closer to equilibrium will decrease the magnitude of the cell potential.	1 point is earned for a justification that relates a lower pressure (or concentration) of $O_2(g)$ to Q, or a qualitative approach using the Nernst equation.

(d) Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

For Na, $1.0 \text{ g Na} \times \frac{1.0 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1.0 \text{ mol } e^-}{1.0 \text{ mol Na}} = 0.043 \text{ mol } e^-$ For Ca, $1.0 \text{ g Ca} \times \frac{1.0 \text{ mol Ca}}{40.08 \text{ g Ca}} \times \frac{2.0 \text{ mol } e^-}{1.0 \text{ mol Ca}} = 0.050 \text{ mol } e^-$ The cell with the Ca anode would transfer more electrons.	1 point is earned for the correct calculation of moles for Na and Ca. 1 point is earned for taking 1 vs. 2 moles of electrons into account and the correct answer.

(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2\ 3d^{10}$ or $[\text{Ar}]\ 4s^2\ 3d^{10}$	1 point is earned for a correct configuration.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

$4s$ sublevel	1 point is earned for the correct answer.

Question 1

Half-Reaction	$E°$ (V)
$2\,CO_2(g) + 12\,H^+(aq) + 12\,e^- \rightarrow C_2H_5OH(aq) + 3\,H_2O(l)$	– 0.085
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	1.229

A student uses a galvanic cell to determine the concentration of ethanol, $C_2H_5OH(aq)$, in an aqueous solution. The cell is based on the half-cell reactions represented in the table above.

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

$C_2H_5OH(aq) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l)$	1 point is earned for the correct reactants and products. 1 point is earned for balancing the equation.

(b) Calculate $E°$ for the overall reaction that occurs in the cell.

$E° = -(-0.085\text{ V}) + 1.229\text{ V} = +1.314\text{ V}$	1 point is earned for a correct answer that is consistent with the equation in part (a).

(c) A 10.0 mL sample of $C_2H_5OH(aq)$ is put into the electrochemical cell. The cell produces an average current of 0.10 amp for 20. seconds, at which point the $C_2H_5OH(aq)$ has been totally consumed.

(i) Calculate the charge, in coulombs, that passed through the cell.

$I = \frac{q}{t} \Rightarrow q = It = 0.10\text{ amp} \times 20.\text{ s} = 2.0\text{ C}$	1 point is earned for the correct charge.

(ii) Calculate the initial $[C_2H_5OH]$ in the solution.

$2.0\text{ C} \times \frac{1\text{ mol }e^-}{96{,}485\text{ C}} \times \frac{1\text{ mol }C_2H_5OH}{12\text{ mol }e^-} = 1.7 \times 10^{-6}\text{ mol }C_2H_5OH$	1 point is earned for the number of moles of C_2H_5OH.
$\frac{1.7 \times 10^{-6}\text{ mol }C_2H_5OH}{10.0\text{ mL}} \times \frac{1000\text{ mL}}{1.0\text{ L}} = 1.7 \times 10^{-4}\ M$	1 point is earned for the initial molarity of C_2H_5OH.

Question 3 (continued)

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

Both Br_2 and I_2 molecules are nonpolar molecules, therefore the only possible intermolecular forces are London dispersion forces. The London dispersion forces are stronger in I_2 because it is larger in size with more electrons and/or a more polarizable electron cloud. The stronger London dispersion forces in I_2 result in a higher melting point,which makes I_2 a solid at room temperature.	1 point is earned for identifying the forces in each substance as London dispersion forces. 1 point is earned for explaining why the forces are stronger in I_2 than in Br_2.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half-reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\,e^- \rightarrow 2\,S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer and include a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $Na_2S_2O_3(aq)$ $Na_2S_4O_6(aq)$

[$Na_2S_2O_3(aq)$ should be circled.] The reaction between $S_2O_3^{2-}(aq)$ and $I_2(s)$ will be thermodynamically favorable because $E°$ for the reaction is positive ($E° = 0.54 - 0.08 = +0.46$ V), from which it follows that $\Delta G°$ is negative because $\Delta G° = -nFE°$.	1 point is earned for the correct choice. 1 point is earned for a correct justification.

(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$	1 point is earned for the correct equation.