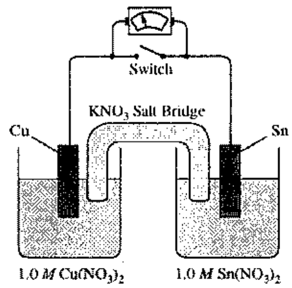
AP® CHEMISTRY
2014 SCORING GUIDELINES

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.

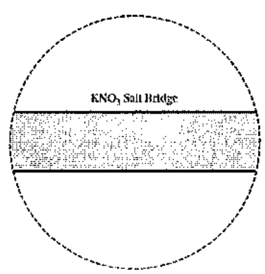
(a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

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.

$E_{cell} = 0.34\text{ V} - (-1.31\text{ V}) = 1.65\text{ V}$	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, $1.0 \text{ g Na} \times \frac{1.0 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1.0 \text{ mol } e^-}{1.0 \text{ mol Na}} = 0.043 \text{ mol } e^-$	1 point is earned for the correct calculation of moles for Na and Ca.
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 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.

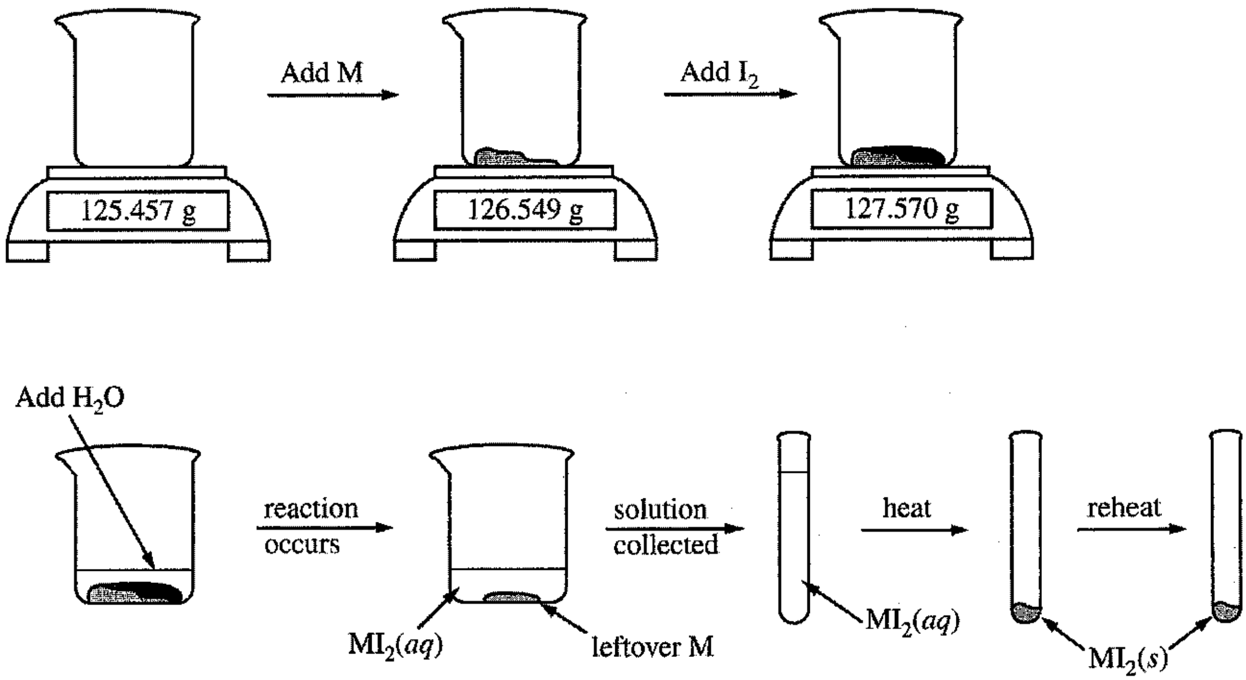
(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

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

Question 3

$$M + I_2 \rightarrow MI_2$$

To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.



Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

Question 3 (continued)

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

$127.570 - 126.549 = 1.021 \text{ g } I_2$ $1.021 \text{ g } I_2 \times \frac{1 \text{ mol } I_2}{253.80 \text{ g } I_2} = 0.004023 \text{ mol } I_2$	1 point is earned for the number of moles.

(b) Calculate the molar mass of the unknown metal M.

Number of moles of I_2 = number of moles of M $1.284 \text{ g } MI_2 - 1.021 \text{ g } I_2 = 0.263 \text{ g M}$ Molar mass of M = $\frac{0.263 \text{ g M}}{0.004023 \text{ mol M}} = 65.4 \text{ g/mol}$	1 point is earned for the number of grams of M. 1 point is earned for the molar mass.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student could dissolve the compound in water or melt the compound and see if the solution/melt conducts electricity. If the solution/melt conducts electricity, mobile ions capable of carrying charge must be present, thus the compound is likely to be ionic. OR The student could heat the compound until it melts or boils. If the melting/boiling point is very high, then the compound is likely to be ionic.	1 point is earned for an appropriate test. 1 point is earned for explaining how the results would support the hypothesis.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

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.

$H_2O_2(aq)$ $\quad$ $Na_2S_2O_3(aq)$ $\quad$ $Na_2S_4O_6(aq)$

[$Na_2S_2O_3(aq)$ 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.

Question 7

A student wants to determine the concentration of H_2O_2 in a solution of $H_2O_2(aq)$. The student can use one of two titrants, either dichromate ion, $Cr_2O_7^{2-}(aq)$, or cobalt(II) ion, $Co^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.

Dichromate as titrant: $Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) + 8\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ O_2(g) + 7\ H_2O(l)$

Cobalt(II) as titrant: $2\ Co^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Co^{3+}(aq) + 2\ H_2O(l)$

The half-reactions and the $E°$ values for the systems related to the titrations above are given in the following table.

Half-Reaction	$E°$ (V) at 298 K
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.84
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$	1.77
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.70

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

(i) $E°$ for the reaction between $Cr_2O_7^{2-}(aq)$ and $H_2O_2(aq)$ at 298 K

$E° = 1.33 - 0.70 = 0.63$ V	1 point is earned for correctly combining $E°$ values.

(ii) $E°$ for the reaction between $Co^{2+}(aq)$ and $H_2O_2(aq)$ at 298 K

$E° = -1.84 + 1.77 = -0.07$ V	1 point is earned for correctly combining $E°$ values.

Question 7 (continued)

(b) Based on the calculated values of $E°$, the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

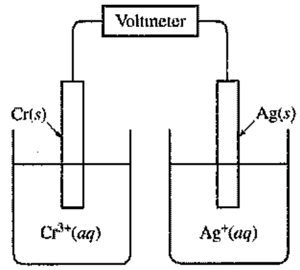
(i) Which titrant should the student choose? Explain your reasoning.

The student should use the dichromate ion for the titration because, for the reaction, the value of $E°$ is positive, which means that the reaction is thermodynamically favorable. OR $\Delta G° = -nFE°$ and n, F, and $E°$ are all positive numbers, therefore $\Delta G° < 0$, which means that the reaction is thermodynamically favorable.	1 point is earned for choosing the correct titrant **and** for understanding that a positive $E°$ or a negative $\Delta G°$ is required.

(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction between the chosen titrant and $H_2O_2(aq)$.

$\Delta G° = -nFE° = -6(96{,}485\,\frac{\text{C}}{\text{mol}})(0.63\,\frac{\text{J}}{\text{C}})(\frac{1\text{ kJ}}{1000\text{ J}}) = -360\text{ kJ/mol}_{rxn}$	1 point is earned for calculating the value of $\Delta G°$.

Question 6



A student sets up a galvanic cell at 298 K that has an electrode of Ag(*s*) immersed in a 1.0 *M* solution of $Ag^+(aq)$ and an electrode of Cr(*s*) immersed in a 1.0 *M* solution of $Cr^{3+}(aq)$, as shown in the diagram above.

(a) The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

The salt bridge is missing. The salt bridge allows for the migration of ions to maintain charge balance in each half-cell.	1 point is earned for the correct answer <u>and</u> a valid explanation.

Half-Reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	?

(b) The student adds the missing component to the cell and measures $E°_{cell}$ to be +1.54 V. As the cell operates, Ag^+ ions are reduced. Use this information and the information in the table above to do the following.

(i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$.

$E°_{cell} = E°_{red}(\text{cathode}) - E°_{red}(\text{anode})$ $+1.54\text{ V} = +0.80\text{ V} - x$ $x = +0.80\text{ V} - (+1.54\text{ V}) = -0.74\text{ V}$	1 point is earned for a correct calculation of $E°_{red}$.

(ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

$3\,Ag^+(aq) + Cr(s) \rightarrow 3\,Ag(s) + Cr^{3+}(aq)$	1 point is earned for the correctly balanced equation.

Question 6 (continued)

(iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol_{rxn}.

$\Delta G° = -nFE° = -\left(\frac{3 \text{ mol } e^-}{1 \text{ mol}_{rxn}}\right)\left(96{,}485 \frac{\text{C}}{\text{mol } e^-}\right)\left(1.54 \frac{\text{J}}{\text{C}}\right)$ $= -4.46 \times 10^5 \text{ J/mol}_{rxn}$	1 point is earned for the correct calculation of the value of $\Delta G°$.