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.

<table>
<thead>
<tr>
<th>Half Reaction</th>
<th>$E$ at pH 11 and 298 K (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 e^- \rightarrow 4 \text{OH}^-(aq)$</td>
<td>0.34</td>
</tr>
<tr>
<td>$\text{ZnO(s)} + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Zn(s)} + 2 \text{OH}^-(aq)$</td>
<td>-1.31</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}_2(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow 2 \text{Na(s)} + 2 \text{OH}^-(aq)$</td>
<td>-1.60</td>
</tr>
<tr>
<td>$\text{CaO(s)} + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Ca(s)} + 2 \text{OH}^-(aq)$</td>
<td>-2.78</td>
</tr>
</tbody>
</table>

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2015 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

(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.

\[ 2 \text{Zn}(s) + \text{O}_2(g) \rightarrow 2 \text{ZnO}(s) \]

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

(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.

(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?

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

(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?

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

(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.

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

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

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?
2. Ethene, \( C_2H_4(g) \) (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, \( C_2H_5OH(g) \) (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.

\[
C_2H_5OH(g) \xrightarrow{\text{catalyst}} C_2H_4(g) + H_2O(g) \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{\text{trans}}; \quad \Delta S^\circ_{298} = 126 \text{ J/(K\cdot mol)}_{\text{trans}}
\]

A student added a 0.200 g sample of \( C_2H_5OH(l) \) to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the \( C_2H_5OH(l) \) evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. (The vapor pressure of water at 305 K is 35.7 torr.)

(a) Calculate the number of moles of \( C_2H_4(g) \)

(i) that are actually produced in the experiment and measured in the gas collection tube and

(ii) that would be produced if the dehydration reaction went to completion.

(b) Calculate the percent yield of \( C_2H_4(g) \) in the experiment.

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

(c) Do the thermodynamic data for the reaction support the student’s claim? Justify your answer, including a calculation of \( \Delta G^\circ_{298} \) for the reaction.
(d) The Lewis electron-dot diagram for \( \text{C}_2\text{H}_4 \) is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for \( \text{C}_2\text{H}_5\text{OH} \) by drawing in all of the electron pairs.

\[
\begin{array}{c}
\text{H} & \text{H} \\
\text{C} & \text{C} \\
\text{H} & \text{H} \\
\end{array}
\quad
\begin{array}{c}
\text{H} & \text{H} \\
\text{H} & \text{C} & \text{C} & \text{O} & \text{H} \\
\text{H} & \text{H} \\
\end{array}
\]

(e) What is the approximate value of the C–O–H bond angle in the ethanol molecule?

(f) During the dehydration experiment, \( \text{C}_2\text{H}_4(g) \) and unreacted \( \text{C}_2\text{H}_5\text{OH}(g) \) passed through the tube into the water. The \( \text{C}_2\text{H}_4 \) was quantitatively collected as a gas, but the unreacted \( \text{C}_2\text{H}_5\text{OH} \) was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.
3. Potassium sorbate, $\text{KC}_6\text{H}_7\text{O}_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $\text{KC}_6\text{H}_7\text{O}_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 $M \text{HCl}(aq)$ using both an indicator and a pH meter. The value of $K_a$ for sorbic acid, $\text{HC}_6\text{H}_7\text{O}_2$, is $1.7 \times 10^{-5}$.

(a) Write the net-ionic equation for the reaction between $\text{KC}_6\text{H}_7\text{O}_2(aq)$ and $\text{HCl}(aq)$.

(b) A total of 29.95 mL of 1.25 $M \text{HCl}(aq)$ is required to reach the equivalence point. Calculate $[\text{KC}_6\text{H}_7\text{O}_2]$ in the stock solution.

(c) The pH at the equivalence point of the titration is measured to be 2.54. Which of the following indicators would be the best choice for determining the end point of the titration? Justify your answer.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>9.3</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>7.0</td>
</tr>
<tr>
<td>Methyl red</td>
<td>5.0</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>2.0</td>
</tr>
<tr>
<td>Methyl violet</td>
<td>0.80</td>
</tr>
</tbody>
</table>

(d) Calculate the pH at the half-equivalence point.
(e) The initial pH and the equivalence point are plotted on the graph below. Accurately sketch the titration curve on the graph below. Mark the position of the half-equivalence point on the curve with an X.

(f) The pH of the soft drink is 3.37 after the addition of the $\text{KC}_6\text{H}_5\text{O}_7(aq)$. Which species, $\text{HC}_6\text{H}_5\text{O}_7$ or $\text{C}_6\text{H}_5\text{O}_7^-$, has a higher concentration in the soft drink? Justify your answer.
4. Answer the following questions about the solubility of \( \text{Ca(OH)}_2 \) \( (K_{sp} = 1.3 \times 10^{-6}) \).

(a) Write a balanced chemical equation for the dissolution of \( \text{Ca(OH)}_2(s) \) in pure water.

(b) Calculate the molar solubility of \( \text{Ca(OH)}_2 \) in 0.10 \( M \) \( \text{Ca(NO}_3\text{)}_2 \).

(c) In the box below, complete a particle representation diagram that includes four water molecules with proper orientation around the \( \text{Ca}^{2+} \) ion.

Represent water molecules as \( \bigcirc \).
5. Blue food coloring can be oxidized by household bleach (which contains OCl\(^-\)) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl\(^-\) is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.

(a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

(b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

(c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?
6. A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

(a) Select two compounds from the table and explain how the data support the student’s hypothesis.

(b) Identify a compound from the table that can be dissolved in water to produce a basic solution. Write the net ionic equation for the reaction that occurs to cause the solution to be basic.
7. Aluminum metal can be recycled from scrap metal by melting the metal to evaporate impurities.

(a) Calculate the amount of heat needed to purify 1.00 mole of Al originally at 298 K by melting it. The melting point of Al is 933 K. The molar heat capacity of Al is 24 J/(mol-K), and the heat of fusion of Al is 10.7 kJ/mol.

(b) The equation for the overall process of extracting Al from $\text{Al}_2\text{O}_3$ is shown below. Which requires less energy, recycling existing Al or extracting Al from $\text{Al}_2\text{O}_3$? Justify your answer with a calculation.

$$\text{Al}_2\text{O}_3 (s) \rightarrow 2 \text{Al}(s) + \frac{3}{2} \text{O}_2 (g) \quad \Delta H^\circ = 1675 \text{ kJ/mol}_\text{mol}$$

STOP

END OF EXAM
\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \\
E_{\text{red}} & = 0.34\text{V} \\
\text{Zn} + 2\text{OH}^- & \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^- \\
E^{\circ}_{\text{ox}} & = 1.31\text{V} \\
E_{\text{cell}} & = E_{\text{red}} + E^{\circ}_{\text{ox}} \\
& = 0.34\text{V} + 1.31\text{V} \\
E^{\circ}_{\text{cell}} & = 1.65\text{V}
\end{align*}
\]
The mass of the cell will increase as oxygen combines with zinc to form ZnO.

\[ \text{bi} \quad 2 \text{Zn} + \text{O}_2 \rightarrow 2 \text{ZnO} \]

\[
\text{65.38 g/mol} \quad 81.58 \text{ g/mol}
\]

The Zn gains mass when it becomes ZnO. Oxygen mass has been added to the cell.

\[ \text{ci} \quad \text{with a lower air pressure the concentration of O}_2 \text{ is less. The cell potential will be lower with a lower reactant concentration.} \]

\[ \text{vi} \quad 2 \text{Zn} + \text{O}_2 = 2 \text{ZnO} \]

a lower O\(_2\) concentration is closer to equilibrium. \( E = 0 \)
d Ca $\rightarrow$ Ca$^{2+} + 2e^-$

there are more moles of

electron available with Ca

$1 \text{g Na} \times \frac{1 \text{mol}}{22.99 \text{g}} \times \frac{1 \text{mole}^-}{1 \text{mol Na}} = 0.043 \text{mol}^-e$

$1 \text{g Ca} \times \frac{1 \text{mol}}{40.08 \text{g}} \times \frac{2 \text{mole}^-}{1 \text{mol Ca}} = 0.05 \text{mol}^-e$

ci 26 Ca \[3d^10\]

ii Electrons are removed from the 4s orbital.
d. \( \text{H} - \text{C} - \text{C} - \text{O} \)  

Bond angle is 105°

c. \( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

f. \( \text{C}_2\text{H}_5\text{OH} \) is capable of \( \text{H} \)-bonding which makes it more soluble in \( \text{H}_2\text{O} \).

\( \text{C}_2\text{H}_4 \) is a nonpolar molecule capable of only induced dipole - dipole attractions with water. It is less soluble in water.
2. \[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

0.200 g C\(_2\)H\(_5\)OH = \( \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.13} \)

\[ \times \frac{1 \text{ mol C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_5\text{OH}} = 4.33 \times 10^{-3} \text{ mol C}_2\text{H}_4 \text{ Theoretical} \]

\[ 35.7 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 4.697 \times 10^{-2} \text{ atm H}_2\text{O} \]

\[ \text{P}_{\text{ethene}} = P_T - P_{\text{H}_2\text{O}} \]

= 0.822 atm - 4.7 \times 10^{-2} \text{ atm}

= 0.775 atm

\[ n = \frac{P \times V}{RT} \]

\[ n = \left( \frac{(0.775 \text{ atm}) \times (0.08548)}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})} \right) \left(305 \text{ K} \right) \]

= 2.64 \times 10^{-3} \text{ mol C}_2\text{H}_4 \text{ actual} \]
2) {b. \% yield = \frac{\text{actual}}{\text{Theoretical}} \times 100

\frac{2.64 \times 10^{-3}}{4.33 \times 10^{-3}} \times 100 = 61.09\%

c. \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ

= 45.5 \text{kJ} - (298 \text{K})(0.126 \text{kJ})

\Delta G^\circ = +7.9 \text{ a positive } \Delta G^\circ\text{ equates to a nonspontaneous reaction. } K_e < 1

3) {a. H^+ + C_6H_7O_2^- \rightarrow HC_6H_7O_2

b. 29.95 \text{ mL} \times \frac{1.25 \text{ mmol HCl}}{1 \text{ mL}} \times \frac{1 \text{ mmol K}_2 \text{C}_6\text{H}_7\text{O}_2}{1 \text{ mmol HCl}}

\times \frac{1}{45 \text{ mL}} = 0.832 \text{ M K}_2 \text{C}_6\text{H}_7\text{O}_2

c. Thymol Blue has a pKa closer to the pH at the equivalence point.
3] \[\begin{align*}
\text{pH} &= \text{pK}_a + \log \left( \frac{[\text{C. base}]}{[\text{Acid}]} \right) \\
\text{pH} &= -\log (1.7 \times 10^{-5}) + \log (1) \\
&= 4.77
\end{align*}\]

\[\begin{align*}
\text{c.} \\
4.77 - \text{max Buffer}
\end{align*}\]

f. \[3.37 = 4.77 + \log \left( \frac{[C_6H_2O_2^-]}{[HC_6H_7O_2]} \right)\]

\[\begin{align*}
\frac{[C_6H_2O_2^-]}{[HC_6H_7O_2]} &= 0.0398 \\
\text{HC}_6\text{H}_7\text{O}_2 \text{ has a greater concentration}
\end{align*}\]
4] \( Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^- \)

a. \( 0.10 \times 2x \)

b. \( K_{sp} = [Ca^{2+}][OH^-]^2 \)

\( 1.3 \times 10^{-6} = (0.10)(2x)^2 \)

\( x = 1.80 \times 10^{-3} \)

C. 

5] a. 1st order

b. Increase the concentration of the Food Color. The reaction will take longer to get to equilibrium.

c. change the settings to a longer wave length (760 nm)
6. a. LiI  \[ \text{M.P.} \quad 449 ^\circ \text{C} \]
   KI  \[ 686 ^\circ \text{C} \]

   K+ is a larger ion than Li+ due to greater shielding of core electrons.

b. \[ \text{NaF(s)} \rightarrow \text{Na}^+ + \text{F}^- \]
   \[ \text{Kb} \]
   \[ \text{F}^- + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}^- \]

7. a. \[ 81 = (1 \text{mol}) \left( \frac{245 \text{ J}}{\text{mol} \cdot \text{K}} \right) \left( 933 - 298 \right) \]
   \[ = 15.24 \text{ kJ} \]

   \[ 82 = (1 \text{mol}) \left( 10.7 \text{ kJ/mol} \right) \]
   \[ = 10.7 \text{ kJ} \]

   \[ 8_T = 8_1 + 8_2 \]
   \[ = 15.24 + 10.7 \]
   \[ = 25.94 \text{ kJ} \]
7/ b. Recycling Al only requires 25.94 kJ/mol to purity it. Extracting Al requires 837.5 kJ/mol. Recyclin requires less energy.

\[
\text{Recycle } 1 \text{ mol Al} \times \frac{25.94 \text{ kJ}}{1 \text{ mol Al}} = 25.94 \text{ kJ}
\]

\[
\text{Extract } 1 \text{ mol Al} \times \frac{1675 \text{ kJ}}{2 \text{ mol Al}} = 837.5 \text{ kJ}
\]