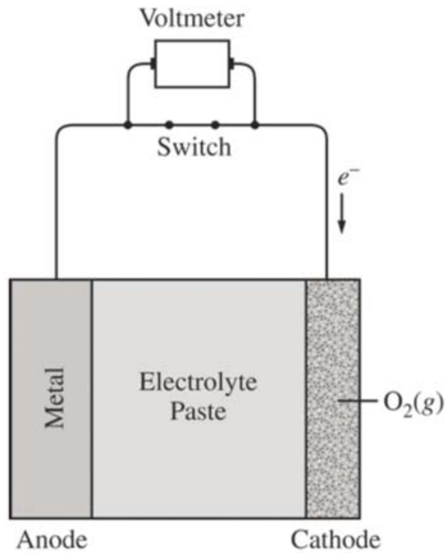
AP® CHEMISTRY 2015 FRQ ANSWERS (submitted by Michael Farabaugh on 05/07/15)

Question 1



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.

The reaction involving ZnO(*s*) should be reversed and multiplied by 2.
This sign of the reduction potential for the half-reaction is changed, but the voltage is <u>not</u> doubled. The reaction involving O_2 does not have to be changed. The two equations are added together to produce the desired overall equation.
The cell potential is equal to (+1.31 V) + (0.34 V) = 1.65 V

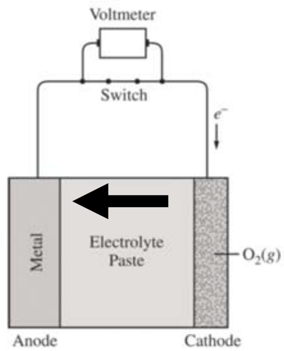
$$2\,Zn(s) + \cancel{4\,OH^-(aq)} \rightarrow 2\,ZnO(s) + \cancel{2\,H_2O(l)} + \cancel{4\,e^-} \qquad E = +1.31\text{ V}$$

$$O_2(g) + \cancel{2\,H_2O(l)} + \cancel{4\,e^-} \rightarrow \cancel{4\,OH^-(aq)} \qquad E = +0.34\text{ V}$$

$$2\,Zn(s) + O_2(g) \rightarrow 2\,ZnO(s) \qquad E = 1.65\text{ V}$$

(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 toward the anode (left).



(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 of the cell increases as the cell operates.

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

The description of the metal-air cell states that it contains "a porous cathode membrane that lets in oxygen from the air." According to the equation for the overall cell reaction, solid zinc reacts with gaseous oxygen to produce solid zinc oxide. The mass of the zinc-air cell should increase as the cell operates because atoms of zinc (in the anode) combine with oxygen atoms (from the air) to produce zinc oxide. The mass of the zinc oxide produced in the cell is heavier than the mass of the original sample of zinc.

(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 on the top of the mountain will be lower than 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.

On top of the mountain, the partial pressure of $O_2(g)$ is less than the partial pressure of $O_2(g)$ at sea level. In the overall cell reaction, $O_2(g)$ is a reactant. In general, decreasing the pressure of a gaseous reactant (or decreasing the concentration of an aqueous reactant) in a galvanic cell will cause the cell potential (E) to decrease from the value that it has under standard conditions.

(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.

Sodium has one valence electron; calcium has two valence electrons.

$$1.0\text{ g Na} \times \frac{1\text{ mol Na}}{22.99\text{ g Na}} \times \frac{1\text{ mol } e^-}{1\text{ mol Na}} = 0.043\text{ mol } e^-$$

$$1.0\text{ g Ca} \times \frac{1\text{ mol Ca}}{40.08\text{ g Ca}} \times \frac{2\text{ mol } e^-}{1\text{ mol Ca}} = 0.050\text{ mol } e^-$$

A 1.0 g anode made of calcium metal is capable of transferring more electrons than a 1.0 g anode made of sodium metal.

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

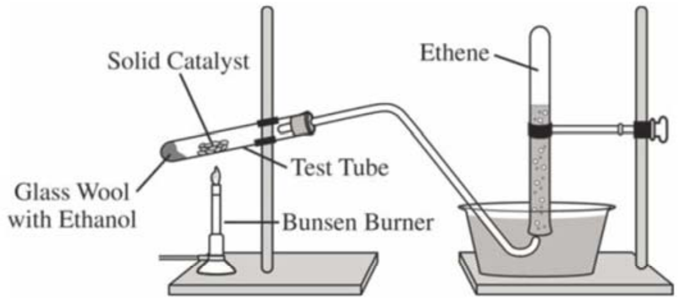
(i) Write the electron configuration for a Zn atom in the ground state.

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ or $[Ar]\ 4s^2 3d^{10}$

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

When a Zn atom in the ground state is oxidized, electrons are removed from the 4s sublevel.

Question 2



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.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{rxn}; \ \Delta S^\circ_{298} = 126 \text{ J/(K}\cdot\text{mol}_{rxn})$$

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

The pressure of the gas collected in the test tube at 305 K = 0.822 atm

$$0.822 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 625 \text{ torr}$$

The vapor pressure of water at 305 K is 35.7 torr
The partial pressure of "dry" $C_2H_4(g)$ is equal to 625 – 35.7 = 589 torr

PV = nRT

$$n = \frac{PV}{RT} = \frac{(589 \text{ torr})(0.0854 \text{ L})}{(62.36 \text{ L torr mol}^{-1} \text{ K}^{-1})(305 \text{ K})} = 2.64\times10^{-3} \text{ mol } C_2H_4$$

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

$$0.200 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.1 \text{ g } C_2H_5OH} \times \frac{1 \text{ mol } C_2H_4}{1 \text{ mol } C_2H_5OH} = 4.34\times10^{-3} \text{ mol } C_2H_4$$

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

$$\text{actual yield of } C_2H_4 = 2.64\times10^{-3}\text{ mol} \times \frac{28.1\text{ g } C_2H_4}{1\text{ mol } C_2H_4} = 0.0742\text{ g } C_2H_4$$

$$\text{theoretical yield of } C_2H_4 = 4.34\times10^{-3}\text{ mol} \times \frac{28.1\text{ g } C_2H_4}{1\text{ mol } C_2H_4} = 0.122\text{ g } C_2H_4$$

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}}\times100\% = \frac{0.0742\text{ g}}{0.122\text{ g}}\times100\% = 60.8\%\text{ yield}$$

OR

$$\text{percent yield} = \frac{2.64\times10^{-3}\text{ mol}}{4.34\times10^{-3}\text{ mol}}\times100\% = 60.8\%\text{ yield}$$

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 ΔG°_{298} for the reaction.

Yes, the thermodynamic data for the reaction support the student's claim.

$$\Delta G^o_{298} = \Delta H^o_{298} - T\Delta S^o_{298}$$

$$= (45.5\text{ kJ/mol}_{rxn}) - (298\text{ K})(0.126\text{ kJ/(K}\bullet\text{mol}_{rxn}))$$

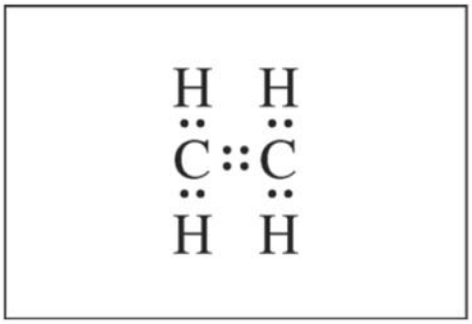
$$= +8.0\text{ kJ/mol}_{rxn}$$

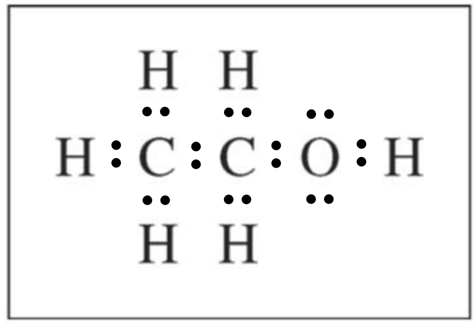
The value of ΔG^o_{298} is positive and based on the following equation

$$\Delta G^o_{298} = -RT\ln K$$

the value of $\ln K$ is negative. Therefore the value of the equilibrium constant K should be less than 1.00 at 298 K.

(d) The Lewis electron-dot diagram for C_2H_4 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for C_2H_5OH by drawing in all of the electron pairs.





Single bonds can also be represented with a dash. —
The two nonbonding pairs of electrons on the oxygen must be included in the Lewis electron-dot diagram.

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

The approximate value of the C–O–H bond angle in the ethanol molecule is 109°. Acceptable bond angles should fall within the range of $105^\circ \leq x \leq 110^\circ$

(f) During the dehydration experiment, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

The C_2H_4 molecule is nonpolar. Water is polar. C_2H_4 only interacts with water via weak London dispersion forces. $C_2H_4(g)$ should not dissolve in the water, so it can be collected quantitatively by water displacement in this experiment.

The C_2H_5OH molecule is polar. It can form strong hydrogen bonding interactions with water molecules. $C_2H_5OH(g)$ should dissolve in the water, so it cannot be collected quantitatively in this experiment.

Question 3

3. Potassium sorbate, $KC_6H_7O_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $KC_6H_7O_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 *M* HCl(*aq*) using both an indicator and a pH meter. The value of K_a for sorbic acid, $HC_6H_7O_2$, is 1.7×10^{-5}.

(a) Write the net-ionic equation for the reaction between $KC_6H_7O_2(aq)$ and HCl(*aq*).

$$C_6H_7O_2^-(aq) + H^+(aq) \rightarrow HC_6H_7O_2(aq)$$

OR

$$C_6H_7O_2^-(aq) + H_3O^+(aq) \rightarrow HC_6H_7O_2(aq) + H_2O(l)$$

(b) A total of 29.95 mL of 1.25 *M* HCl(*aq*) is required to reach the equivalence point. Calculate $[KC_6H_7O_2]$ in the stock solution.

$$0.02995\text{ L} \times \frac{1.25\text{ mol HCl}}{1\text{ L}} \times \frac{1\text{ mol }KC_6H_7O_2}{1\text{ mol HCl}} \times \frac{1}{0.04500\text{ L}} = 0.832\ M$$

OR

Since there is a 1-to-1 molar relationship between the $KC_6H_7O_2$ (base) and the HCl (acid) at the equivalence point,

$$M_bV_b = M_aV_a$$

$$M_b = \frac{M_aV_a}{V_b} = \frac{(1.25\ M\text{ HCl})(29.95\text{ mL})}{(45.00\text{ mL})} = 0.832\ M$$

(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.

Indicator	pK_a
Phenolphthalein	9.3
Bromothymol blue	7.0
Methyl red	5.0
Thymol blue	2.0
Methyl violet	0.80

The best indicator to use is the one for which the value of pK_a is closest to the pH at the equivalence point. Thymol blue is the best choice, since its pK_a value (2.0) is closest to the pH value of 2.54.

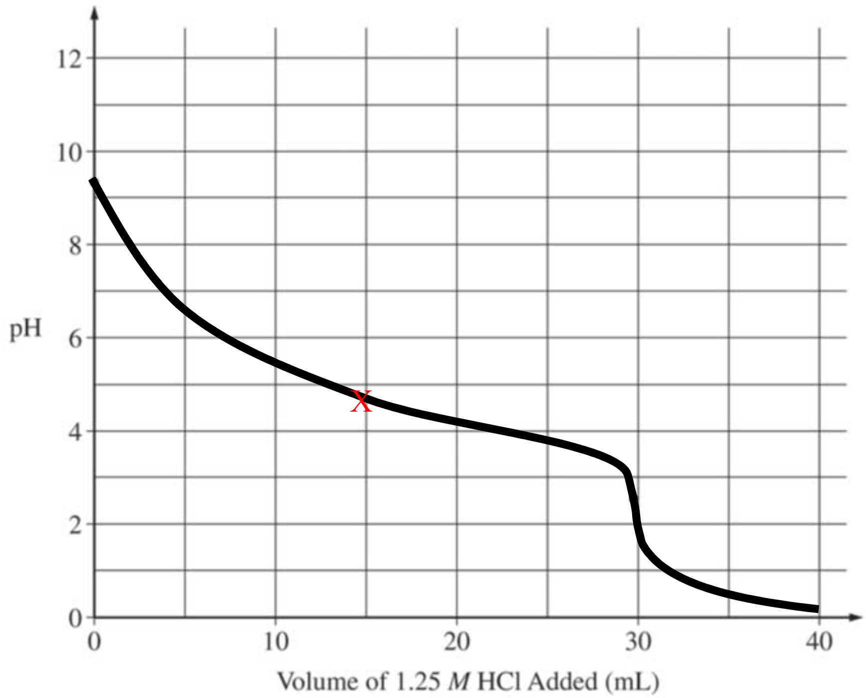
(d) Calculate the pH at the half-equivalence point.

$$K_a = \frac{[H^+][C_6H_7O_2^-]}{[HC_6H_7O_2]} = 1.7\times 10^{-5}$$

At the half-equivalence point, $[C_6H_7O_2^-] = [HC_6H_7O_2]$ and $pH = pK_a$.

$pK_a = -\log(1.7\times 10^{-5}) = 4.77$

(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.



Note that point "X" should occur at a volume of 15 mL <u>and</u> the pH should be consistent with the student's answer to part (d).

(f) The pH of the soft drink is 3.37 after the addition of the $KC_6H_7O_2(aq)$. Which species, $HC_6H_7O_2$ or $C_6H_7O_2^-$, has a higher concentration in the soft drink? Justify your answer.

$HC_6H_7O_2$ has a higher concentration in the soft drink than $C_6H_7O_2^-$

$\text{pH} = 3.37 = -\log[H^+]$

$[H^+] = 10^{-3.37} = 4.3 \times 10^{-4}\ M$

$$K_a = \frac{[H^+][C_6H_7O_2^-]}{[HC_6H_7O_2]} = \frac{(4.3 \times 10^{-4})\,[C_6H_7O_2^-]}{[HC_6H_7O_2]} = 1.7 \times 10^{-5}$$

$\dfrac{[C_6H_7O_2^-]}{[HC_6H_7O_2]} = 0.040$ This ratio < 1, so $[HC_6H_7O_2] > [C_6H_7O_2^-]$

OR

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

$$3.37 = 4.77 + \log\frac{[C_6H_7O_2^-]}{[HC_6H_7O_2]}$$

$$-1.40 = \log\frac{[C_6H_7O_2^-]}{[HC_6H_7O_2]}$$

The log of $\dfrac{[C_6H_7O_2^-]}{[HC_6H_7O_2]}$ is negative, so this ratio < 1 and $[HC_6H_7O_2] > [C_6H_7O_2^-]$

Question 4

4. Answer the following questions about the solubility of $Ca(OH)_2$ ($K_{sp} = 1.3 \times 10^{-6}$).

(a) Write a balanced chemical equation for the dissolution of $Ca(OH)_2(s)$ in pure water.

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$$

(b) Calculate the molar solubility of $Ca(OH)_2$ in 0.10 *M* $Ca(NO_3)_2$.

Let x = molar solubility of $Ca(OH)_2$

$[Ca^{2+}] = x$ and $[OH^-] = 2x$

$K_{sp} = [Ca^{2+}][OH^-]^2 = 1.3 \times 10^{-6}$

$[Ca^{2+}] = 0.10\ M$ in a 0.10 *M* solution of $Ca(NO_3)_2$

$K_{sp} = (0.10 + x)[OH^-]^2 = 1.3 \times 10^{-6}$

Assuming that $x << 0.10\ M$

$K_{sp} = (0.10)[OH^-]^2 = 1.3 \times 10^{-6}$

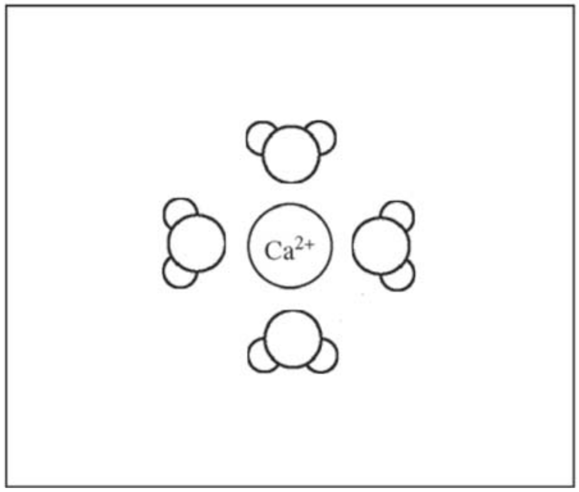
$[OH^-]^2 = 1.3 \times 10^{-5}$

$[OH^-] = \sqrt{1.3 \times 10^{-5}} = 3.6 \times 10^{-3}\ M = 2x$

molar solubility of $Ca(OH)_2 = x = 1.8 \times 10^{-3}\ M$

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

Represent water molecules as .

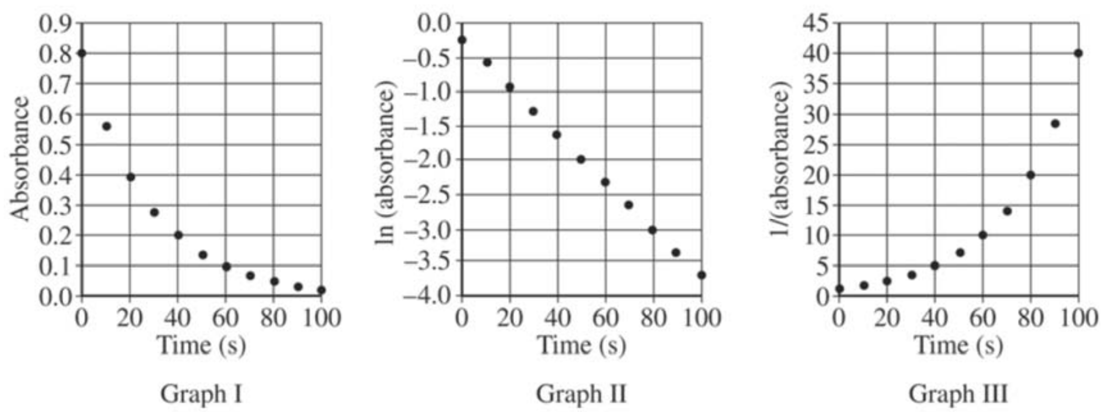


The negative end (oxygen atom) of each water molecule should be oriented toward the positive Ca^{2+} ion.

Question 5

$$\underset{blue}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \rightarrow \underset{colorless}{\text{products}}$$

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?

The order of the reaction with respect to the blue food coloring is first order.

(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.

This is a first-order reaction. The half-life (time required for half of the sample to decay) is a constant value. By increasing the initial concentration of the food coloring in the reaction mixture, the initial value for the absorbance will increase. If the experiment is started at a higher absorbance value, it should take a longer 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?

The spectrophotometer was set at a wavelength of 635 nm during the experiment that measured the absorbance of blue food coloring. In order to measure the absorbance of red food coloring, the wavelength on the spectrophotometer should be changed to a different value. (e.g., a wavelength of 500 nm).

Question 6

Compound	Melting Point (°C)
LiI	449
KI	686
LiF	845
NaF	993

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.

Compare LiF with NaF.

The ionic radius of the Li^+ cation is smaller than the ionic radius of the Na^+ cation.
The ionic radius of the I^- anion is larger than the ionic radius of the F^- anion.
The melting point of LiI is less than the melting point of NaF.

This data supports the hypothesis is that if a salt is composed of small cations and large anions, it should have a relatively low melting point.

(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.

Either LiF or NaF could have been chosen.
The fluoride ion acts as a weak base in water.

$F^-(aq) + H_2O(l) \rightarrow HF(aq) + OH^-(aq)$

Question 7

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.

Heat required to raise the temperature of 1.00 mol Al from 298 K to 933 K:

(1.00 mol)(24 J/(mol•K)(933 K – 298 K) = 15200 J = 15.2 kJ

Heat required to melt 1.00 mol Al at 933 K:

(1.00 mol)(10.7 kJ/mol) = 10.7 kJ

Total heat needed to purify 1.00 mol Al = 15.2 kJ + 10.7 kJ = 25.9 kJ

(b) The equation for the overall process of extracting Al from Al_2O_3 is shown below. Which requires less energy, recycling existing Al or extracting Al from Al_2O_3 ? Justify your answer with a calculation.

$$Al_2O_3(s) \rightarrow 2\,Al(s) + \frac{3}{2}O_2(g) \qquad \Delta H^\circ = 1675\ \text{kJ/mol}_{rxn}$$

The amount of heat required to extract Al(*s*) from Al_2O_3(*s*) is

$$\frac{1675\ \text{kJ}}{2\ \text{mol Al}} = \frac{838\ \text{kJ}}{1\ \text{mol Al}}$$

It requires less energy to recycle existing aluminum (25.9 kJ/mol) than it does to extract aluminum from aluminum oxide (838 kJ/mol).