AP®

AP® Chemistry
2015 Scoring Guidelines

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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.

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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.

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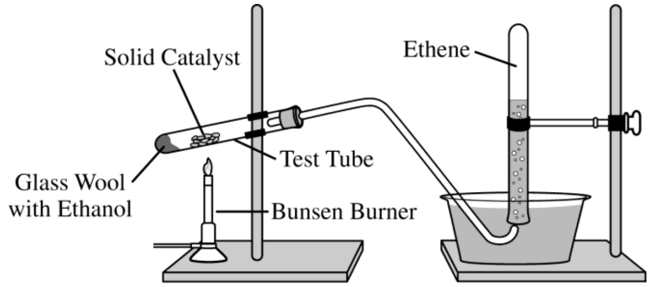
Question 2



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.

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

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

$35.7 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.0470 \text{ atm}$ $P_{\text{ethene}} = P_{\text{total}} - P_{\text{water}} = 0.822 \text{ atm} - 0.0470 \text{ atm} = 0.775 \text{ atm}$	1 point is earned for the calculation of the pressure of the dry ethene.
$n = \frac{PV}{RT} = \frac{(0.775 \text{ atm})(0.0854 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(305 \text{ K})} = 0.00264 \text{ mol}$	1 point is earned for the correct number of moles of ethene gas.

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

$0.200 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.1 \text{ g } C_2H_5OH} \times \frac{1 \text{ mol } C_2H_4}{1 \text{ mol } C_2H_5OH}$ $= 0.00434 \text{ mol } C_2H_4 \text{ produced}$	1 point is earned for the correct number of moles of ethene produced.

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

$\%\text{ yield} = \frac{\text{actual yield}}{\text{maximum possible yield}} \times 100 = \frac{0.00264 \text{ mol}}{0.00434 \text{ mol}} \times 100 = 60.8\%$	1 point is earned for the correct percent yield.

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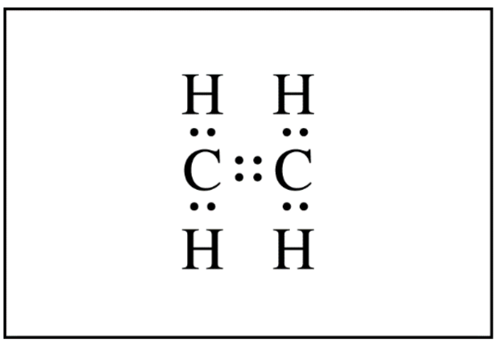
Question 2 (continued)

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 data support the student's claim. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= 45.5\ \text{kJ/mol}_{rxn} - (298\ \text{K})(0.126\ \text{kJ/(K·mol}_{rxn})) = 8.0\ \text{kJ/mol}_{rxn}$ Because $\Delta G^\circ > 0$, the value of $K_p = e^{(\frac{-\Delta G^\circ}{RT})} < 1.00$.	1 point is earned for the correct calculation of ΔG°. 1 point is earned for a valid justification.

(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.



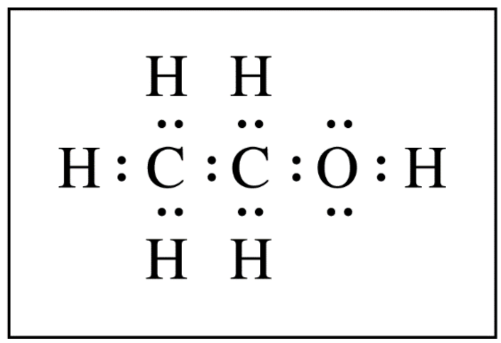


Diagram should include all bonding pairs plus two nonbonding pairs on the O atom. (A line may be used to represent an electron pair.)	1 point is earned for a correct diagram.

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

The bond angle is approximately 109°.	1 point is earned for an angle from 100° to 115°.

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Question 2 (continued)

(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.

Ethene is only slightly soluble in water because the weak dipole/induced dipole intermolecular attractions between nonpolar ethene molecules and polar water molecules are weaker than the hydrogen bonds between water molecules. Ethanol molecules are soluble in water because they are polar and form hydrogen bonds with water molecules as they dissolve.	1 point is earned for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of differences in polarity. 1 point is earned for describing the intermolecular forces between ethene and water as weak dipole/induced dipole forces and attributing the solubility of ethanol in water to the hydrogen bonds formed between ethanol molecules and water molecules.

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Question 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 $HCl(aq)$.

$H^+ + C_6H_7O_2^- \rightleftarrows HC_6H_7O_2$	1 point is earned the net-ionic equation.

(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.

$\frac{1.25 \text{ mol HCl}}{1000 \text{ mL}} = \frac{x \text{ mol HCl}}{29.95 \text{ mL}} \quad x = 0.0374 \text{ mol HCl}$	1 point is earned for the moles of HCl at the equivalence point.
$\frac{0.0374 \text{ mol } C_6H_7O_2^-}{45.0 \text{ mL}} = \frac{x \text{ mol } C_6H_7O_2^-}{1000 \text{ mL}} \Rightarrow 0.832\ M$	1 point is earned for the correct answer.

(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

Thymol blue; it has a pK_a close to the pH at the equivalence point, so it will change color near the equivalence point.	1 point is earned for the correct indicator. 1 point is earned for correct justification.

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

$pH = pK_a = -\log(1.7 \times 10^{-5}) = 4.77$	1 point is earned for the correct pH.

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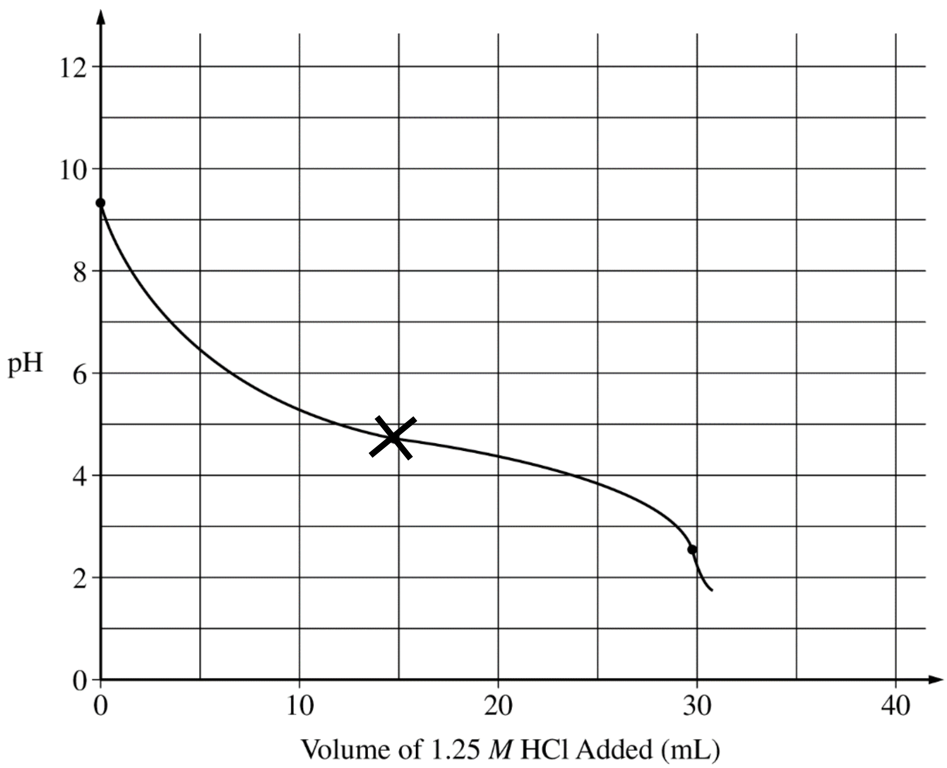
Question 3 (continued)

(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.



[The pH curve should have the correct shape.]	1 point is earned for a half-equivalence point consistent with the answer to part (d) and at the correct volume. 1 point is earned for a curve that levels off to a relatively horizontal slope through the half-equivalence point. 1 point is earned for a relatively steep negative slope through the equivalence point.

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Question 3 (continued)

(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.

For sorbic acid, $K_a = \dfrac{[H^+][C_6H_7O_2^-]}{[HC_6H_7O_2]}$, thus $\dfrac{[C_6H_7O_2^-]}{[HC_6H_7O_2]} = \dfrac{K_a}{[H^+]} = \dfrac{1.7 \times 10^{-5}}{10^{-3.37}} \approx 0.04$ $\Rightarrow$ $[HC_6H_7O_2] > [C_6H_7O_2^-]$ **OR** The concentrations of $HC_6H_7O_2$ and $C_6H_7O_2^-$ are equal at the half-equivalence point. A pH of 3.37 is lower than that at the half-equivalence point, so the protonated form, $HC_6H_7O_2$, has a higher concentration in the soft drink.	1 point is earned for identifying the correct species <u>and</u> for making a comparison involving the pH (with or without calculation).

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Question 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.

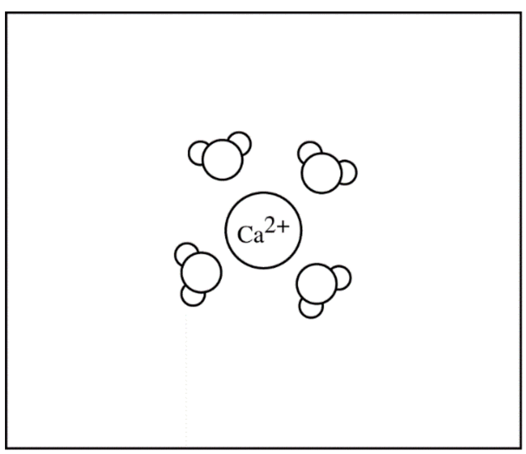
$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2\ OH^-$	1 point is earned for the correct equation.

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

$K_{sp} = [Ca^{2+}]\,[OH^-]^2$ $1.3 \times 10^{-6} = (0.10 + x)\,(2x)^2 \approx (0.10)\,4x^2$ [assuming $x << 0.10$] $1.3 \times 10^{-5} = 4x^2$ $x = 0.0018\ M$ Molar solubility of $Ca(OH)_2 = 0.0018\ M$	1 point is earned for the correct stoichiometry and setup. 1 point is earned for the final answer.

(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 diagram should show the oxygen side of the water molecules oriented closer to the Ca^{2+} ion.]	1 point is earned for a correct diagram that shows at least three of the four water molecules oriented as described.

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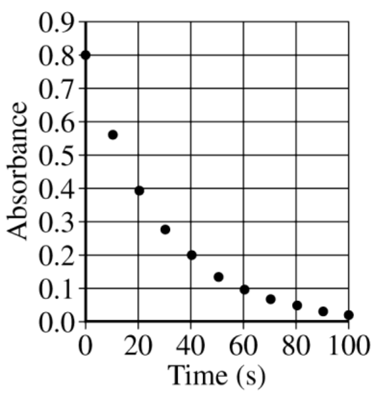
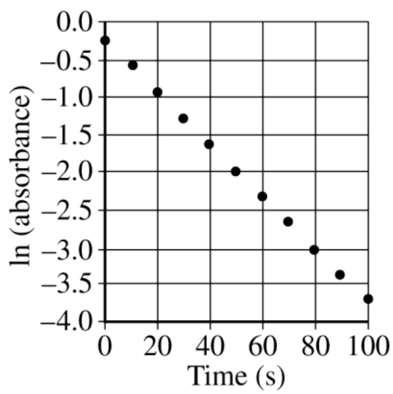
Question 5

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

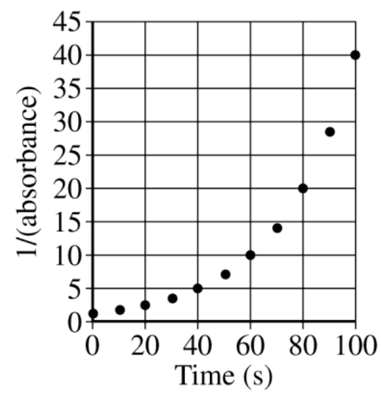
Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the 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.



Graph I



Graph II



Graph III

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

First order	1 point is earned for the correct 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.

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Question 5 (continued)

[“Increasing the concentration of the food coloring” should be circled.]	1 point is earned for the correct choice.
If the initial concentration of blue food coloring is increased, then more time is required (regardless of the reaction order indicated in part (a)) for the bleach to oxidize the additional blue food coloring.	1 point is earned for a correct explanation.

(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 should be set to a different wavelength.	1 point is earned for a correct answer.

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Question 6

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

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.

LiI and KI. LiI has a small cation and a large anion and KI has a large cation and the same large anion. The melting point of LiI (with its smaller cation) is lower than that of KI. **OR** LiI and LiF. LiI has a small cation and a large anion and LiF has the same small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of LiF. **OR** LiI and NaF. LiI has a small cation and a large anion and NaF has a relatively small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of NaF.	1 point is earned for choosing an appropriate pair of compounds (LiI/KI, LiI/LiF, or LiI/NaF). 1 point is earned for an explanation that supports the 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.

Either LiF or NaF is acceptable. $F^- + H_2O \rightleftarrows HF + OH^-$	1 point is earned for choosing one of the correct compounds. 1 point is earned for writing a correct balanced equation.

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Question 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.

To raise the temperature from 298 K to 933 K: $q = \frac{24\text{ J}}{\text{mol K}} \times 1.00\text{ mol} \times 635\text{ K} = 15{,}000\text{ J} = 15\text{ kJ}$ It takes 10.7 kJ to melt the Al at 933 K. 15 kJ + 10.7 kJ = 26 kJ	1 point is earned for calculating the amount of heat needed to raise the temperature to 933 K. 1 point is earned for adding the heat of fusion to the previous result to get a final answer.

(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.

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

For extracting Al from ore: $1675\text{ kJ/mol}_{rxn} \times \frac{1\text{ mol of reaction}}{2\text{ mol Al}} = 837.5\text{ kJ per mol of Al}$ Producing 1.00 mol of Al from Al_2O_3 requires 837.5 kJ. Because 26 kJ < 837.5 kJ, recycling requires less energy.	1 point is earned for a calculation to get equal numbers of moles for comparison. 1 point is earned for a correct comparison.

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