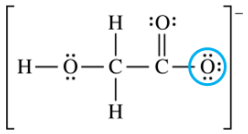
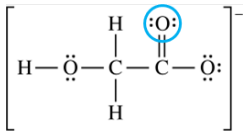
Question 7: Short Answer — 4 points

A For a correct circled atom. **Point 01**

Accept one of the following:

- 
- 

(Because of resonance, the two C–O *bonds on the right are equivalent.)*

B (i) For the correct calculated value: **Point 02**

$$K_b = \frac{[HC_2H_3O_3][OH^-]}{[C_2H_3O_3^-]} = \frac{(1.3\times10^{-5})(1.3\times10^{-5})}{(2.5-1.3\times10^{-5})} \approx \frac{(1.3\times10^{-5})^2}{(2.5)} = 6.8\times10^{-11}$$

(ii) For the correct calculated value, consistent with part B (i): **Point 03**

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{6.8\times10^{-11}} = 1.5\times10^{-4}$$

C For the correct answer and a valid justification: **Point 04**

Agree. H_3O^+ *is consumed in step 1 and regenerated in step 2, which is consistent with the behavior of a catalyst.*

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Question

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

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.

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.

SCORING GUIDELINES

Question 1 (continued)

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 lower pressure (or concentration) of O_2(or a qualitative approach using the Nernst equation.

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.

Na, $1.0\text{ g Na} \times \frac{1.0\text{ mol Na}}{22.99\text{ g Na}} \times \frac{1.0\text{ mol } e^-}{1.0\text{ mol Na}} = 0.043\text{ mol } e^-$ 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 1 point is earned for taking 1 vs. 2 moles of electrons into account the correct answer.

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] $4s^2\,3d^{10}$	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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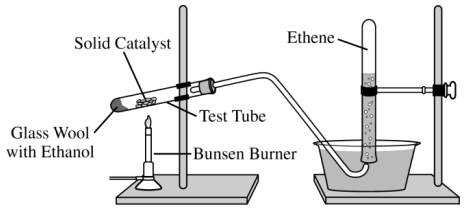
Question



Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH($ (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.)

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

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

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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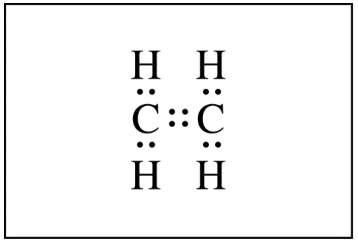
Question 2 (continued)

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.

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 $K_p = e^{\left(\frac{-\Delta G^\circ}{RT}\right)} < 1.00$.	1 point is earned for the correct calculation of Δ 1 point is earned for a valid justification.

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.



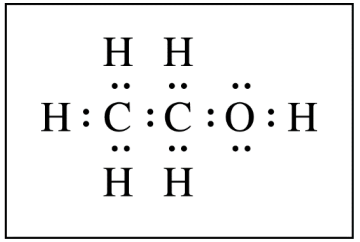


Diagram should include all bonding pairs plus two nonbonding pairs on the O atom. (A line may be used to represent an electron pair.)	1 point is earned for a correct diagram.

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 (continued)

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.

2015 SCORING GUIDELINES

Question

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, H_7O_2, is 1.7×10^{-5}.

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.

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

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

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.

Calculate the pH at the half-equivalence point.

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

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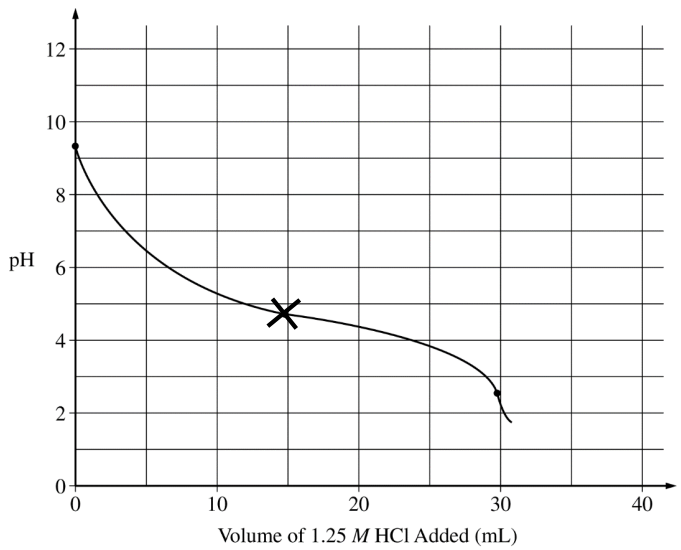
Question 3 (continued)

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



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)

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, $K_a = \frac{[H^+][C_6H_7O_2^-]}{[HC_6H_7O_2]}$, thus $\frac{[C_6H_7O_2^-]}{[HC_6H_7O_2]} = \frac{K_a}{[H^+]} = \frac{1.7 \times 10^{-5}}{10^{-3.37}} \approx 0.04$ $\Rightarrow [HC_6H_7O_2] > [C_6H_7O_2^-]$ 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 and for making a comparison involving the pH (with or without calculation).

2015 SCORING GUIDELINES

Question

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

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

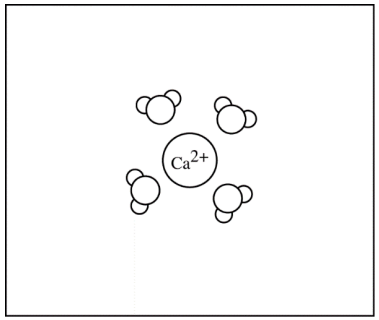
$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2\ OH^-$	1 point is earned for the correct equation.

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

$= [Ca^{2+}]\,[OH^-]^2$ $\therefore 10^{-6} = (0.10 + x)\,(2x)^2 \approx (0.10)\,4x^2$ [assuming $x << 0.10$] $\therefore 10^{-5} = 4x^2$ $= 0.0018\ M$ 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 fi answer.

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

Represent water molecules as 



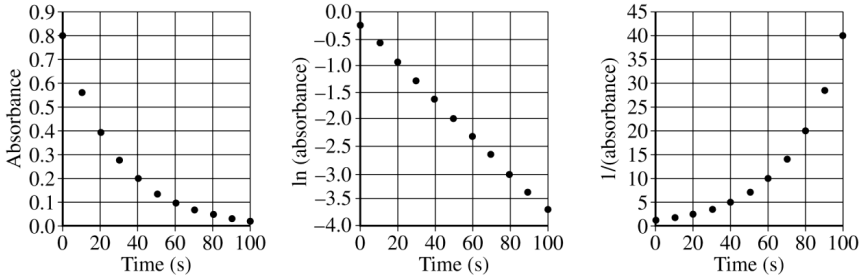
[The diagram should show the oxygen side of the water molecules oriented closer to the Ca^{2+} ion.]	1 point is earned for a correct diagram that shows at least three of the four water molecules oriented as described.

2015 SCORING GUIDELINES

Question

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

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

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.

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 ntinued)

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

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.

2015 SCORING GUIDELINES

Question

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.

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. 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. 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.

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

2015 SCORING GUIDELINES

Question

Aluminum metal can be recycled from scrap metal by melting the metal to evaporate impurities.

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: $= \frac{24\ \text{J}}{\text{mol K}} \times 1.00\ \text{mol} \times 635\ \text{K} = 15{,}000\ \text{J} = 15\ \text{kJ}$ It takes 10.7 kJ to melt the Al at 933 K. J + 10.7 kJ = 26 kJ	1 point is earned for calculating the amount 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.

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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4 SCORING GUIDELINES

Question 1
(10 points)

Mass of KI tablet	0.425 g
Mass of thoroughly dried filter paper	1.462 g
Mass of filter paper + precipitate after first drying	1.775 g
Mass of filter paper + precipitate after second drying	1.699 g
Mass of filter paper + precipitate after third drying	1.698 g

A student is given the task of determining the I^- content of tablets that contain KI and an inert, water-soluble sugar as a filler. A tablet is dissolved in 50.0 mL of distilled water, and an excess of 0.20 *M* $Pb(NO_3)_2(aq)$ is added to the solution. A yellow precipitate forms, which is then filtered, washed, and dried. The data from the experiment are shown in the table above.

(a) For the chemical reaction that occurs when the precipitate forms,

(i) write a balanced, net-ionic equation for the reaction, and

$Pb^{2+} + 2\,I^- \rightarrow PbI_2$	1 point is earned for a balanced net-ionic equation.

(ii) explain why the reaction is best represented by a net-ionic equation.

The net-ionic equation shows the formation of the $PbI_2(s)$ from $Pb^{2+}(aq)$ and $I^-(aq)$ ions, omitting the non-reacting species (spectator ions), $K^+(aq)$ and $NO_3^-(aq)$.	1 point is earned for a valid explanation.

(b) Explain the purpose of drying and weighing the filter paper with the precipitate three times.

The filter paper and precipitate must be dried several times (to a constant mass) to ensure that all the water has been driven off.	1 point is earned for a valid explanation.

(c) In the filtrate solution, is $[K^+]$ greater than, less than, or equal to $[NO_3^-]$? Justify your answer.

$[K^+]$ is less than $[NO_3^-]$ because the source of the NO_3^-, the 0.20 *M* $Pb(NO_3)_2(aq)$, was added in excess.	1 point is earned for a correct comparison with a valid explanation.

4 SCORING GUIDELINES

Question 1 (continued)

(d) Calculate the number of moles of precipitate that is produced in the experiment.

$1.698\text{ g} - 1.462\text{ g} = 0.236\text{ g } PbI_2(s)$ $0.236\text{ g } PbI_2 \times \frac{1\text{ mol } PbI_2}{461.0\text{ g } PbI_2} = 5.12 \times 10^{-4}\text{ mol } PbI_2$	1 point is earned for the correct number of moles of $PbI_2(s)$ precipitate.

(e) Calculate the mass percent of I^- in the tablet.

$5.12 \times 10^{-4}\text{mol } PbI_2 \times \frac{2\text{ mol } I^-}{1\text{ mol } PbI_2} = 1.02 \times 10^{-3}\text{mol } I^-$ $1.02 \times 10^{-3}\text{mol } I^- \times \frac{126.91\text{ g } I^-}{1\text{ mol } I^-} = 0.130\text{ g } I^-\text{ in one tablet}$ $\frac{0.130\text{ g } I^-}{0.425\text{ g KI tablet}} = 0.306 = 30.6\%\ I^-\text{ per KI tablet}$	1 point is earned for determining the number of moles of I^- in one tablet. 1 point is earned for calculating the mass percent of I^- in the KI tablet.

(f) In another trial, the student dissolves a tablet in 55.0 mL of water instead of 50.0 mL of water. Predict whether the experimentally determined mass percent of I^- will be greater than, less than, or equal to the amount calculated in part (e). Justify your answer.

The mass percent of I^- will be the same. $Pb^{2+}(aq)$ was added in excess, ensuring that essentially no I^- remained in solution. The additional water is removed by filtration and drying, leaving the same mass of dried precipitate.	1 point is earned for correct comparison with a valid justification.

(g) A student in another lab also wants to determine the I^- content of a KI tablet but does not have access to $Pb(NO_3)_2$. However, the student does have access to 0.20 *M* $AgNO_3$, which reacts with $I^-(aq)$ to produce $AgI(s)$. The value of K_{sp} for AgI is 8.5×10^{-17}.

(i) Will the substitution of $AgNO_3$ for $Pb(NO_3)_2$ result in the precipitation of the I^- ion from solution? Justify your answer.

Yes. Addition of an excess of 0.20 *M* $AgNO_3(aq)$ will precipitate all of the I^- ion present in the solution because AgI is insoluble, as evidenced by its low value of K_{sp}.	1 point is earned for the correct answer with a valid justification.

(ii) The student only has access to one KI tablet and a balance that can measure to the nearest 0.01 g. Will the student be able to determine the mass of AgI produced to three significant figures? Justify your answer.

4 SCORING GUIDELINES

Question 1 (continued)

No. If masses can be measured to ±0.01 g, then the mass of the dry $AgI(s)$ precipitate (which is less than 1 g) will be known to only two significant figures.	1 point is earned for a correct answer with a valid justification.

2014 SCORING GUIDELINES

Question (10 points)

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

CH_3CH_2COOH and $CH_3CH_2COO^-$ *acid* *base* OR H_3O^+ and H_2O *acid* *base*	1 point is earned for writing (or naming) either of the Brønsted-Lowry conjugate acid-base pairs with a clear indication of which is the acid and which is the base.

(b) Determine the value of K_a for propanoic acid at 25°C.

$[H_3O^+] = 10^{-pH} = 10^{-2.79} = 1.6 \times 10^{-3}\ M$ $[CH_3CH_2COO^-] = [H_3O^+]$ AND $[CH_3CH_2COOH] = 0.20\ M - [H_3O^+]$, OR $[CH_3CH_2COOH] \approx 0.20\ M$ (state or assume that $[H_3O^+] << 0.20\ M$) $K_a = \frac{[CH_3CH_2COO^-][H_3O^+]}{[CH_3CH_2COOH]} = \frac{(1.6 \times 10^{-3}\ M)^2}{0.20\ M} = 1.3 \times 10^{-5}$	1 point is earned for correctly solving for $[H_3O^+]$. 1 point is earned for the K_a expression for propanoic acid OR 1 point is earned for substituting values into the K_a expression. 1 point is earned for correctly solving for the value of K_a.

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 *M* CH_3CH_2COOH with a 50.0 mL sample of 0.20 *M* NaOH is 7.00.

False. The conjugate base of a weak acid undergoes hydrolysis (see equation below) at equivalence to form a solution with a pH > 7. $\left(CH_3CH_2COO^- + H_2O \rightleftarrows CH_3CH_2COOH + OH^-\right)$	1 point is earned for noting that the statement is false AND providing a supporting explanation.

2014 SCORING GUIDELINES

Question 2 (continued)

(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

True. HCl is a strong acid that ionizes completely. Fewer moles of HCl are needed to produce the same $[H_3O^+]$ as the propanoic acid solution, which only partially ionizes.	1 point is earned for noting that the statement is true and providing a supporting explanation.

A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 *M* NaOH solution is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 *M* NaOH, reaching the end point after 20.52 mL of the base solution has been added.

(d) Calculate the molarity of the propanoic acid solution.

Let x = moles of propanoic acid then $x = (0.02052 \text{ L NaOH}) \times \frac{0.173 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol acid}}{1 \text{ mol NaOH}}$ $= 3.55 \times 10^{-3}$ mol propanoic acid $\frac{3.55 \times 10^{-3} \text{ mol acid}}{0.02500 \text{ L acid}} = 0.142 \ M$ OR Since CH_3CH_2COOH is monoprotic and, at the equivalence point, moles H^+ = moles OH^-, then $M_A V_A = M_B V_B$ $M_A = \frac{M_B V_B}{V_A} = \frac{(0.173 \ M \text{ NaOH})(20.52 \text{ mL NaOH})}{25.00 \text{ mL acid}} = 0.142 \ M$	1 point is earned for correctly calculating the number of moles of acid that reacted at the equivalence point. 1 point is earned for the correct molarity of acid.

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

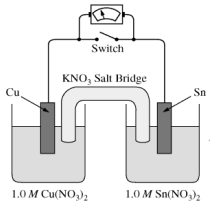
2014 SCORING GUIDELINES

Question 2 (continued)

Disagree with the student's claim From part (b) above, pK_a for propanoic acid is $\log(1.3 \times 10^{-5}) = 4.89$. Because 4.83 is so close to 4.89, the pH at the equivalence point in the titration of butanoic acid should be close enough to the pH in the titration of propanoic acid to make the original indicator appropriate for the titration of butanoic acid.	1 point is earned for disagreeing with the student's claim and making a valid justification using pK_a, K_a, or pH arguments. 1 point is earned for numerically comparing either: the two pK_a values, the two K_a values, or the two pH values at the equivalence point.

SCORING GUIDELINES

Question (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.

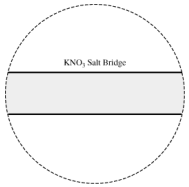
(a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

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.

SCORING GUIDELINES

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
$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$	0.34
$Sn^{4+} + 2\,e^- \rightarrow Sn^{2+}$	0.15
$Sn^{2+} + 2\,e^- \rightarrow Sn(s)$	–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.

SCORING GUIDELINES

Question 3 (continued)

$Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$ $E°$ 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 the correct net-ionic equation. 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.

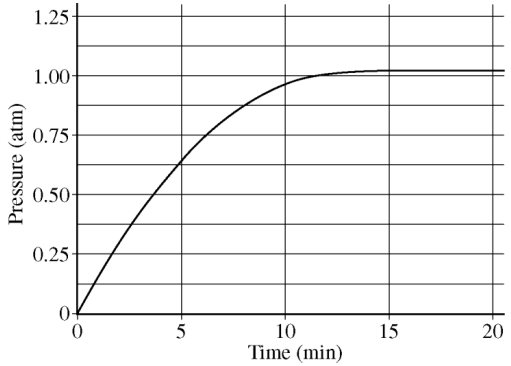
$\Delta G° = -nFE°$ $\Delta G^\circ = -\frac{2 \text{ mol } e^-}{\text{mol}_{rxn}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{0.48 \text{ J}}{\text{C}} = -93{,}000 \text{ J/mol}_{rxn} = -93 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct number of electrons. 1 point is earned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

SCORING GUIDELINES

Question
(4 points)

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $CaCO_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $CaCO_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

(a) Calculate the number of moles of $CO_2(g)$ present in the container after 20 minutes of heating.

$PV = nRT$ $\frac{PV}{RT} = n = \frac{(1.04 \text{ atm})(1.00 \text{ L})}{(0.0821 \frac{\text{L atm}}{\text{mol K}})(1100 \text{ K})} = 0.0115 \text{ mol } CO_2$	1 point is earned for the proper setup using the ideal gas law and an answer that is consistent with the setup.

SCORING GUIDELINES

Question continued)

(b) The student claimed that the final pressure in the container in each experiment became constant because all of the $CaCO_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.

Do not agree with claim Explanation I: In experiment 1, the moles of $CaCO_3$ = 50.0 g/100.09 g/mol = 0.500 mol $CaCO_3$. If the reaction had gone to completion, 0.500 mol of CO_2 would have been produced. From part (a) only 0.0115 mol was produced. Hence, the student's claim was false. Explanation II: The two different experiments (one with 50.0 g of $CaCO_3$ and one with 100.0 g of $CaCO_3$) reached the same constant, final pressure of 1.04 atm. Since increasing the amount of reactant did not produce more product, there is no way that all of the $CaCO_3$ reacted. Instead, an equilibrium condition has been achieved and there must be some solid $CaCO_3$ in the container.	1 point is earned for disagreement with the claim and for a correct justification using stoichiometry or a discussion of the creation of an equilibrium condition.

(c) After 20 minutes some $CO_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

The final pressure would be equal to 1.04 atm. Equilibrium was reached in both experiments; the equilibrium pressure at this temperature is 1.04 atm. As the reaction shifts toward the reactant, the amount of $CO_2(g)$ in the container will decrease until the pressure returns to 1.04 atm.	1 point is earned for the correct answer with justification.

(d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p, for the decomposition of $CaCO_3(s)$ at 1100 K? Justify your answer.

SCORING GUIDELINES

Question continued)

Yes. For the equilibrium reaction represented by the chemical equation in this problem, at a given temperature the equilibrium pressure of CO_2 determines the equilibrium constant. Since the measured pressure of CO_2 is also the equilibrium pressure of CO_2, $K_p = P_{CO_2} = 1.04$. Note: If the response in part (b) indicates "yes" , that all of the $CaCO_3(s)$ had decomposed, then the point can be earned by stating that the system did not reach equilibrium in either experiment and hence the value of K_p cannot be calculated from the data.	1 point is earned for correct explanation that is consistent with the student's answer to part (b).

SCORING GUIDELINES

Question 5
(4 points)

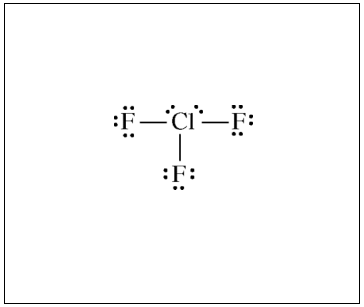
Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF_4	NF_3	OF_2	No compound	SiF_4	PF_3	SF_2	No compound

Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

(a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?

ClF	1 point is earned for the correct formula.

(b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF_3. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF_3.



See diagram above.	1 point is earned for a central Cl atom surrounded by three bonding pairs with F atoms and two nonbonding (lone) pairs of electrons. F atoms must have three nonbonding pairs each. Electron pairs can be depicted as dots or line segments.

SCORING GUIDELINES

Question 5 (continued)

(c) Two possible geometric shapes for the ClF_3 molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF_3 molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

The molecule is T-shaped because a T-shaped structure is asymmetric with dipoles that do not cancel out, but produce a net dipole (i.e., a polar molecule). OR because, if the molecule had a trigonal planar structure, the molecule would be symmetric with dipoles that cancel out and produce a net dipole of zero (i.e., a nonpolar molecule), which is not consistent with the observation that the ClF_3 molecule does have a dipole moment.	1 point is earned for indicating that the molecule is T-shaped with an acceptable explanation.

In an attempt to resolve the existence of the ClF_3 molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

Halogen	Formula(s)
F	F_2
Cl	
Br	BrF, BrF_3, BrF_5
I	IF, IF_3, IF_5, IF_7

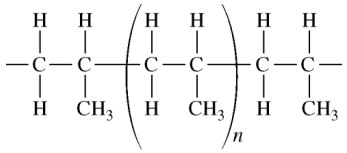
(d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

An acceptable hypothesis (descriptive or formulaic) must include the following ideas: 1. Atomic Structure: e.g., odd number of F atoms 2. Periodicity: e.g., as the atomic number of the central halogen atom increases, the number of F atoms increases.	1 point is earned for an acceptably modified hypothesis that addresses both atomic structure and periodicity.

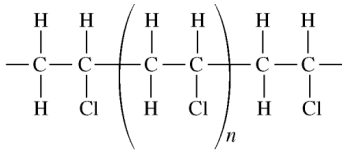
SCORING GUIDELINES

Question
(4 points)

A student places a mixture of plastic beads consisting of polypropylene (PP) and polyvinyl chloride (PVC) in a 1.0 L beaker containing distilled water. After stirring the contents of the beaker vigorously, the student observes that the beads of one type of plastic sink to the bottom of the beaker and the beads of the other type of plastic float on the water. The chemical structures of PP and PVC are represented by the diagrams below, which show segments of each polymer.



PP

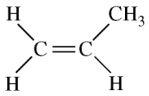


PVC

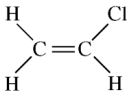
(a) Given that the spacing between polymer chains in PP and PVC is similar, the beads that sink are made of which polymer? Explain.

The PVC beads sink. The spacing between chains is similar, but a Cl atom has a greater mass than CH_3.	1 point is earned for the correct polymer with a correct explanation.

PP is synthesized from propene, C_3H_6, and PVC is synthesized from vinyl chloride, C_2H_3Cl. The structures of the molecules are shown below.



Propene



Vinyl Chloride (chloroethene)

(b) The boiling point of liquid propene (226 K) is lower than the boiling point of liquid vinyl chloride (260 K). Account for this difference in terms of the types and strengths of intermolecular forces present in each liquid.

Both substances have dipole-dipole interactions and London dispersion forces (or propene is essentially nonpolar with only LDFs while vinyl chloride has both LDFs and dipole-dipole forces). Propene contains a CH_3 group, but vinyl chloride contains a Cl atom. Vinyl chloride thus has a larger electron cloud, is more polarizable, and has a larger dipole moment. Thus intermolecular attractions are stronger in vinyl chloride, which results in it having the higher boiling point.	1 point is earned for a discussion of intermolecular forces and for a comparison of their relative strengths.

SCORING GUIDELINES

Question 6 (continued)

In a separate experiment, the student measures the enthalpies of combustion of propene and vinyl chloride. The student determines that the combustion of 2.00 mol of vinyl chloride releases 2300 kJ of energy, according to the equation below.

$$2\ C_2H_3Cl(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(g) + 2\ HCl(g) \qquad \Delta H^\circ = -2300\ \text{kJ/mol}_{rxn}$$

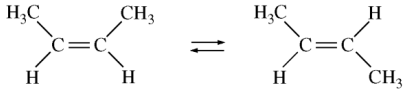
(c) Using the table of standard enthalpies of formation below, determine whether the combustion of 2.00 mol of propene releases more, less, or the same amount of energy that 2.00 mol of vinyl chloride releases. Justify your answer with a calculation. The balanced equation for the combustion of 2.00 mol of propene is $2\ C_3H_6(g) + 9\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g)$.

Substance	$C_2H_3Cl(g)$	$C_3H_6(g)$	$CO_2(g)$	$H_2O(g)$	$HCl(g)$	$O_2(g)$
Standard Enthalpy of Formation (kJ/mol)	37	21	–394	–242	–92	0

$\Delta H^\circ = 6(-394) + 6(-242) - 2(21) = -3858\ \text{kJ/mol}_{rxn}$ The combustion of 2.00 mol of propene releases more energy.	1 point is earned for the calculation of the enthalpy of combustion of propene. 1 point is earned for the comparison of propene to vinyl chloride that is consistent with the calculated value.

SCORING GUIDELINES

Question 7
(4 points)



cis-2-butene *trans*-2-butene

The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

For a first-order reaction, the half-life is independent of reactant concentration (or pressure) at constant T, as shown in trials 1, 2, and 3.	1 point is earned for a correct explanation.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100.\text{ s}} = 0.00693\text{ s}^{-1}$	1 point is earned for correct numerical answer with units.

(c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2 ? Justify your answer.

The initial rate in trial 1 is less than that in trial 2 because rate = k [*cis*-2-butene] or rate = $k\,P_{cis\text{-}2\text{-butene}}$ (with reference to values from both trials). OR because the initial concentration of *cis*-2-butene in trial 1 is less than that in trial 2 and k is constant.	1 point is earned for the correct answer with justification.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

The temperature is higher in trial 4, meaning that the KE_{avg} of the molecules is greater. Consequently, in this trial a greater fraction of collisions have sufficient energy to overcome the activation energy barrier, thus the rate is greater.	1 point is earned for a correct answer with justification.