AP® Chemistry
2014 Scoring Guidelines

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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.

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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.

$5.12 \times 10^{-4}\text{ mol } PbI_2 \times \frac{2\text{ mol } I^-}{1\text{ mol } PbI_2} = 1.02 \times 10^{-3}\text{ mol } I^-$ $1.02 \times 10^{-3}\text{ mol } I^- \times \frac{126.91\text{ g } I^-}{1\text{ mol } I^-} = 0.130\text{ g } I^-$ in one tablet $\frac{0.130\text{ g } I^-}{0.425\text{ g KI tablet}} = 0.306 = 30.6\%\ I^-$ 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.

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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.

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Question 2
(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. $(CH_3CH_2COO^- + H_2O \rightleftarrows CH_3CH_2COOH + OH^-)$	1 point is earned for noting that the statement is false AND providing a supporting explanation.

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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.

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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.

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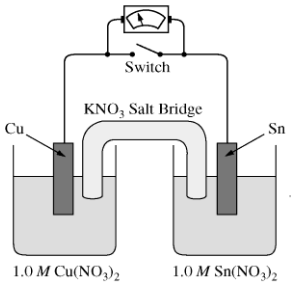
Question 3
(10 points)



A student is given a standard galvanic cell, represented above, that has a Cu electrode and a Sn electrode. As current flows through the cell, the student determines that the Cu electrode increases in mass and the Sn electrode decreases in mass.

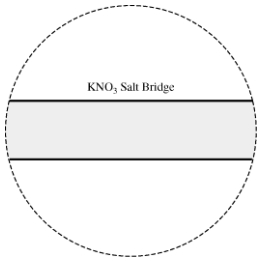
(a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

Since the Sn electrode is losing mass, Sn atoms must be forming $Sn^{2+}(aq)$. This process is oxidation. OR because the cell operates, $E°$ must be positive and, based on the $E°$ values from the table, it must be Sn that is oxidized.	1 point is earned for the correct answer with justification.

(b) As the mass of the Sn electrode decreases, where does the mass go?

The atoms on the Sn electrode are going into the solution as Sn^{2+} ions.	1 point is earned for the correct answer.

(c) In the expanded view of the center portion of the salt bridge shown in the diagram below, draw and label a particle view of what occurs in the salt bridge as the cell begins to operate. Omit solvent molecules and use arrows to show the movement of particles.



The response should show at least one K^+ ion moving toward the Cu compartment on the left and at least one NO_3^- ion moving in the opposite direction.	1 point is earned for correct representation of both K^+ and NO_3^- ions. (Including free electrons loses this point.) 1 point is earned for correctly indicating the direction of movement of both ions.

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Question 3 (continued)

(d) A nonstandard cell is made by replacing the 1.0 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$ in the standard cell with 0.50 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$. The volumes of solutions in the nonstandard cell are identical to those in the standard cell.

(i) Is the cell potential of the nonstandard cell greater than, less than, or equal to the cell potential of the standard cell? Justify your answer.

It is the same. In the cell reaction $Q = \frac{[Sn^{2+}]}{[Cu^{2+}]}$, and the concentrations of Sn^{2+} and Cu^{2+} are equal to each other in both cases.	1 point is earned for the correct answer with justification.

(ii) Both the standard and nonstandard cells can be used to power an electronic device. Would the nonstandard cell power the device for the same time, a longer time, or a shorter time as compared with the standard cell? Justify your answer.

The nonstandard cell would power the device for a shorter time because the supply of Cu^{2+} ions will be exhausted more quickly. OR The nonstandard cell would power the device for a shorter time because the reaction will reach $E = 0$ more quickly.	1 point is earned for the correct answer with justification.

(e) In another experiment, the student places a new Sn electrode into a fresh solution of 1.0 *M* $Cu(NO_3)_2$.

Half-Reaction	$E°$ (V)
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	–0.14

(i) Using information from the table above, write a net-ionic equation for the reaction between the Sn electrode and the $Cu(NO_3)_2$ solution that would be thermodynamically favorable. Justify that the reaction is thermodynamically favorable.

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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.

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

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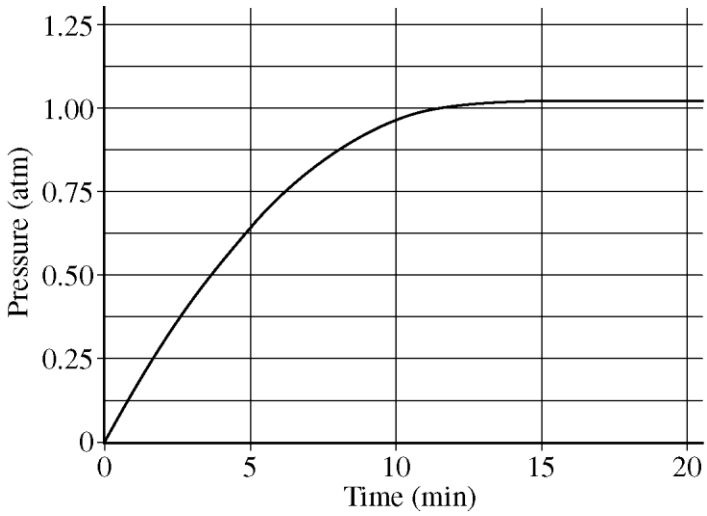
Question 4
(4 points)

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

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.

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Question 4 (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 <u>and</u> 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.

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Question 4 (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).

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Question 5
(4 points)

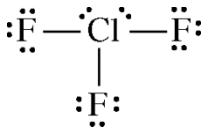
Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF_4	NF_3	OF_2	No compound	SiF_4	PF_3	SF_2	No compound

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.

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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.

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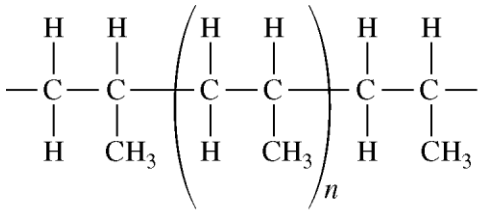
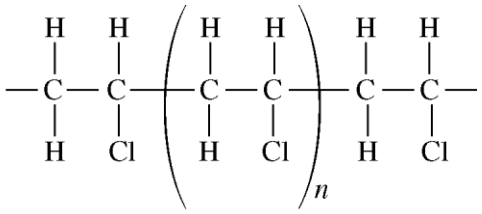
Question 6
(4 points)

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

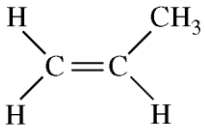


PVC

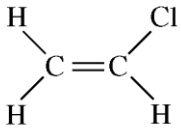
(a) Given that the spacing between polymer chains in PP and PVC is similar, the beads that sink are made of which polymer? Explain.

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 <u>and</u> for a comparison of their relative strengths.

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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.

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

(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

$\Delta H° = 6(-394) + 6(-242) - 2(21) = -3858\ \text{kJ/mol}_{rxn}$ 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.

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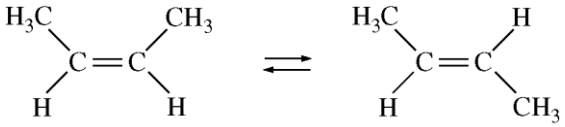
Question 7
(4 points)



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 $P_{cis\text{-2-butene}}$ (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 = $k\,P_{cis\text{-2-butene}}$ (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.

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