Question 2: Long Answer — 10 points

(a) For the correct calculated value reported with the correct number of significant figures: **1 point**

$$1.25 \text{ mol } AlCl_3 \times \frac{3 \text{ mol Cl}}{1 \text{ mol } AlCl_3} \times \frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}} = 133 \text{ g Cl}$$

(b) For the correct algebraic manipulation of either ΔH_2° or ΔH_4° (may be implicit): **1 point**

Accept one of the following:

- *Reversing reaction 2:*

  $AlCl_3(g) \rightarrow Al(s) + \frac{3}{2}Cl_2(g) \quad \Delta H_{rxn}^\circ = -(-583) = +583 \text{ kJ/mol}_{rxn}$

- *Multiplying reaction 4 by* $\frac{3}{2}$*:*

  $\frac{3}{2}(Cl_2(g) \rightarrow 2\,Cl(g)) \quad \Delta H_{rxn}^\circ = \frac{3}{2}(+243) = +365 \text{ kJ/mol}_{rxn}$

For the correct calculated value: **1 point**

$$\Delta H_1^\circ = -\Delta H_2^\circ + \Delta H_3^\circ + 1.5(\Delta H_4^\circ) = -(-583) + 326 + 1.5(243) = 1274 \text{ kJ/mol}_{rxn}$$

Total for part (b) 2 points

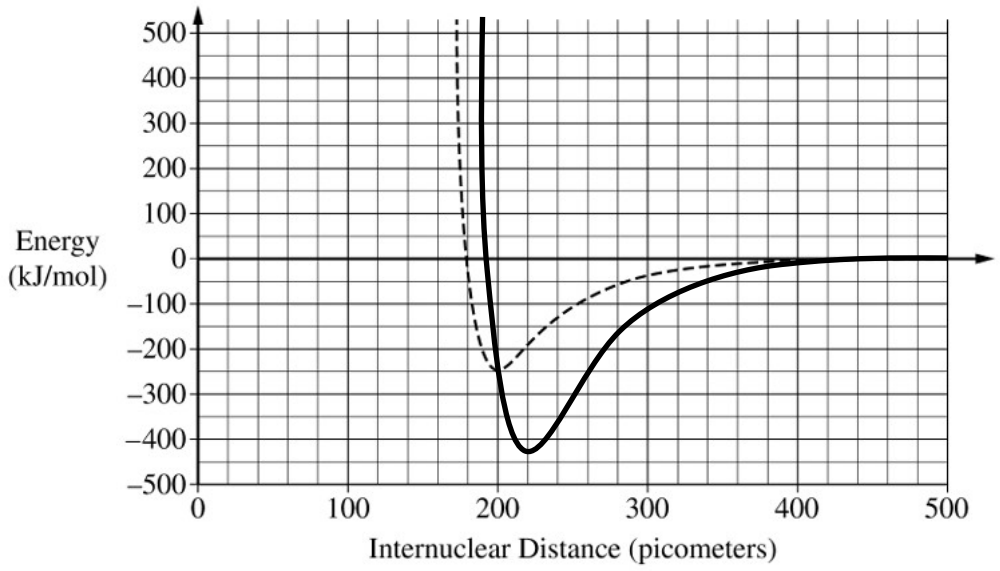
(c) (i) For the correct answer: **1 point**

200 picometers (±10 pm)

(ii) For a curve with a minimum at an internuclear distance of 220 ± 10 pm: **1 point**

See sample curve below

For a curve with a minimum energy value of -425 ± 20 kJ/mol that approaches zero as the internuclear distance approaches 500 pm: **1 point**



Total for part (c) 3 points

(d) (i)	For the correct answer and a valid justification: *Diagram 2. Al has four electron domains in Diagram 2, which would be trigonal pyramidal, not trigonal planar.*	**1 point**
(ii)	For the correct answer and a valid justification: *Diagram 1. All atoms in diagram 1 have a formal charge of zero, whereas atoms in diagrams 2 and 3 have nonzero formal charges.*	**1 point**
	Total for part (d)	**2 points**
(e)	For the correct answer: $K_p = \frac{P_{Al_2Cl_6}}{(P_{AlCl_3})^2}$	**1 point**
(f)	For the correct calculated value, consistent with part (e): $K_p = \frac{\chi_{Al_2Cl_6}(P_{total})}{\left(\chi_{AlCl_3}(P_{total})\right)^2} = \frac{\frac{3}{10}(22.1)}{\left(\frac{7}{10}(22.1)\right)^2} = 0.0277$	**1 point**
	Total for question 2	**10 points**

2017

AP® CollegeBoard

AP Chemistry

Scoring Guidelines

2017 SCORING GUIDELINES

Question 1

$$CS_2(g) + 3\ Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(g)$$

Carbon tetrachloride, $CCl_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.

(a) Chlorine gas, $Cl_2(g)$, is initially present in the container at a pressure of 0.40 atm.

(i) How many moles of $Cl_2(g)$ are in the container?

$n = \frac{PV}{RT} = \frac{0.40\ \text{atm} \times 25.0\ \text{L}}{0.08206\ (\text{L} \cdot \text{atm})/(\text{mol} \cdot \text{K}) \times 393\ \text{K}} = 0.31\ \text{mol}\ Cl_2(g)$	1 point is earned for the correct answer with supporting work.

(ii) How many grams of carbon disulfide, $CS_2(g)$, are needed to react completely with the $Cl_2(g)$?

$0.31\ \text{mol}\ Cl_2 \times \frac{1\ \text{mol}\ CS_2}{3\ \text{mol}\ Cl_2} \times \frac{76.13\ \text{g}\ CS_2}{1\ \text{mol}\ CS_2} = 7.9\ \text{g}\ CS_2$	1 point is earned for using the correct mole ratio (may be implicit). 1 point is earned for the mass of CS_2.

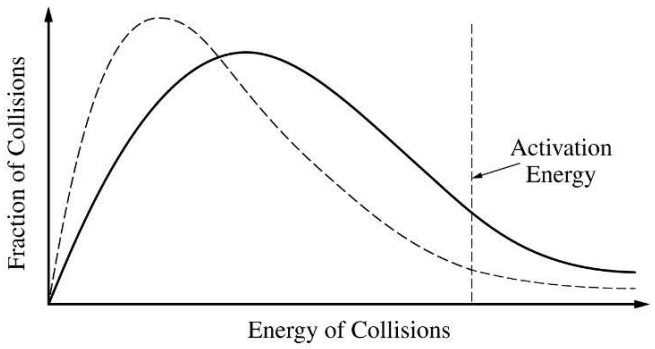
(b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C, the reaction occurs at an observable rate.

(i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C.

At the higher temperature the particles have a greater average kinetic energy than at the lower temperature. Thus there are more collisions with sufficient energy to overcome the activation energy.	1 point is earned for an appropriate explanation that includes a reference to molecular collisions.

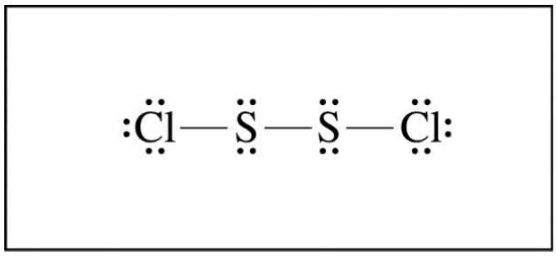
(ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C. Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C.

Question 1 (continued)

	1 point is earned for a curve that has a peak above and to the left of the given curve. 1 point is earned for a curve that is below the given curve in the region beyond the activation energy.

(c) S_2Cl_2 is a product of the reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.



See correct diagram above.	1 point is earned for a correctly drawn diagram.

(ii) What is the approximate value of the Cl–S–S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl–S–S bond angles are not equal, include both angles.)

Any value between 104° and 110°	1 point is earned for an acceptable angle that is consistent with the Lewis diagram.

(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

Question 1 (continued)

(i) Identify all types of intermolecular forces present in $HCl(l)$.

Dipole-dipole forces, London dispersion forces	1 point is earned for both types of forces.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

The intermolecular forces among CCl_4 molecules must be **stronger** than those among HCl molecules because the CCl_4 condenses at a higher temperature than HCl.	1 point is earned for the correct answer with a valid justification.

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Question 2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

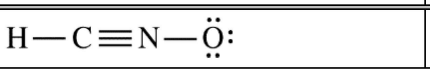
(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of –1. In the diagram on the right, the C atom has a formal charge of –1 and the O atom has a formal charge of zero.	1 point is earned for a correct assignment of formal charges in the two diagrams.
The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon.	1 point is earned for a correct explanation.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
	

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

Compound	HCNO	HNCO
Bond Enthalpies (kJ/mol)	413 + 891 + 201	391 + 615 + 745
Total Bond Enthalpy (kJ/mol)	1505	1751

$\Delta H^\circ = \Sigma(\text{enthalpies of bonds broken}) - \Sigma(\text{enthalpies of bonds formed})$

$= 1505 \text{ kJ/mol} - 1751 \text{ kJ/mol}$

$= -246 \text{ kJ/mol}_{rxn}$

1 point is earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken.

1 point is earned for the correct determination of ΔH°.

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Question 2 (continued)

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

The change from fulminic acid to isocyanic acid is a rearrangement of atoms with no change in phase or number of molecules.	1 point is earned for a correct explanation.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

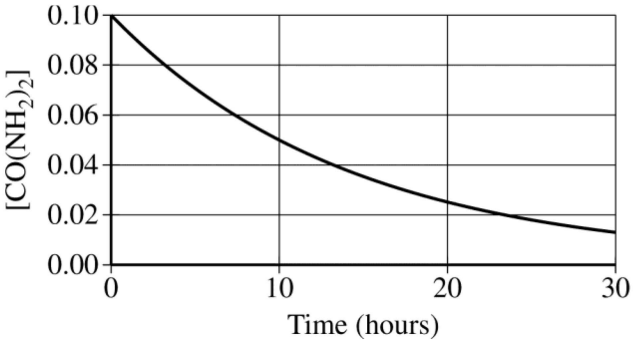
Isocyanic acid (HNCO) will be present in higher concentration. $\Delta G°$ is essentially equal to $\Delta H°$ because $\Delta S°$ is essentially zero, so $\Delta G° \approx -246$ kJ/mol$_{rxn}$, indicating the forward reaction is thermodynamically favorable. Since $\Delta G°$ is negative, $K > 1$ ($\Delta G° = -RT \ln K$), resulting in a higher concentration of product than reactant at equilibrium.	1 point is earned for the correct choice **with** a valid justification. (Calculation of $\Delta G°$ is a sufficient justification.) 1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



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Question 2 (continued)

(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

From inspecting the data table or the graph, it is evident that the decomposition reaction has a constant half-life, which indicates that the reaction is a first-order reaction.	1 point is earned for a correct explanation.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

Since the reaction is first order, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.\text{ h}} = 0.069\text{ h}^{-1}$ OR $k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.1000) - \ln(0.0500)}{10.\text{ h}} = 0.069\text{ h}^{-1}$	1 point is earned for the correct value of k with correct units.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

Perform the experiment at a different concentration of $OH^-(aq)$ and measure how the concentration of $CO(NH_2)_2$ changes over time. (Other variables, such as temperature, should be held constant.)	1 point is earned for the description of a valid experiment.

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Question 3

$$N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$$

At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

$K_p = \dfrac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$	1 point is earned for a correct K_p expression.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

	$N_2(g) + O_2(g) \rightleftarrows$		$2\ NO(g)$
Initial	6.01	1.61	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$6.01-x$	$1.61-x$	0.122

$2x = 0.122$ atm $\Rightarrow$ $x = 0.0610$ atm

$K_p = \dfrac{(0.122)^2}{(5.95)(1.55)} = 0.00161$

1 point is earned for the correct equilibrium partial pressures of reactants and products (may be implicit).

1 point is earned for the correct calculation of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids, such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 *M* $HNO_2(aq)$ and 0.100 *M* $NaOH(aq)$.

(i) Explain why the addition of 0.100 *M* $NaOH(aq)$ to 0.100 *M* $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

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Question 3 (continued)

NaOH will neutralize some of the HNO_2 to produce NO_2^-. The resulting solution contains a mixture of a weak acid and its conjugate base, which is a buffer solution. $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$	1 point is earned for the recognition that the solution produced is a mixture of a weak acid and its conjugate base. 1 point is earned for the correct net ionic equation.

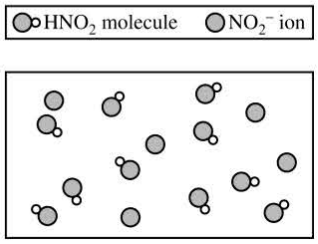
(ii) Determine the volume, in mL, of 0.100 *M* NaOH(*aq*) the student should add to 100. mL of 0.100 *M* HNO_2(*aq*) to make a buffer solution with a pH of 3.40. Justify your answer.

The student should add 50.0 mL of 0.100 *M* NaOH(*aq*). When half of the HNO_2 is converted to the conjugate base, $[HNO_2] = [NO_2^-]$, therefore the buffer has a pH equal to pK_a. OR $pH = pK_a + \log \frac{[NO_2^-]}{[HNO_2]}$, thus $pH = pK_a$ when $[HNO_2] = [NO_2^-]$	1 point is earned for the correct volume. 1 point is earned for clearly indicating a 1 to 1 ratio of HNO_2 and NO_2^- (calculation not required).

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2$(*s*) in 100. mL of 1.00 *M* HNO_2(*aq*). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

The buffer made by the second student is more resistant to changes in pH because it contains a higher concentration of HNO_2 and NO_2^- to react with added H^+ or OH^- ions.	1 point is earned for the correct choice and a valid justification.

(e) A new buffer is made using HNO_2(*aq*) as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.



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Question 3 (continued)

The pH of the solution is less than 3.40. If $[HNO_2] = [NO_2^-]$, pH = pK_a, and the pH of the solution would be 3.40. Since $[HNO_2] > [NO_2^-]$, as represented in the diagram, the solution has a pH less than 3.40. OR $pH = pK_a + \log \frac{[NO_2^-]}{[HNO_2]} \Rightarrow pH = 3.40 + \log \frac{5}{10} \Rightarrow pH = 3.10$	1 point is earned for the correct choice. 1 point is earned for a valid justification.

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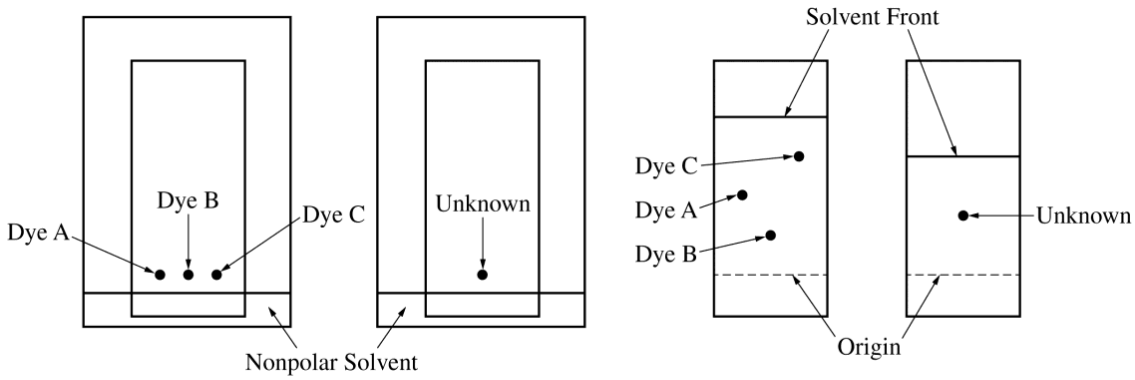
Question 4



Chromatography Chambers

Developed Chromatograms

A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.

(a) Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

Dye C is the least polar because it moved the farthest. Nonpolar dyes are more strongly attracted to the nonpolar solvent. AND/OR Nonpolar dyes are least strongly retained by the polar paper.	1 point is earned for the correct choice **and** reference to the chromatogram. 1 point is earned for a correct description of dye-solvent **and/or** dye-paper interactions.

(b) Which dye is present in the unknown sample? Justify your answer.

Dye A is present in the unknown sample. The unknown sample moves to a position that is midway between the origin and the solvent front, and so does dye A. OR Dye A has a retention factor (R_f) that is close to 0.50 on the chromatogram with the three dyes, and the unknown also has a retention factor close to 0.50.	1 point is earned for the correct choice. 1 point is earned for a valid justification.

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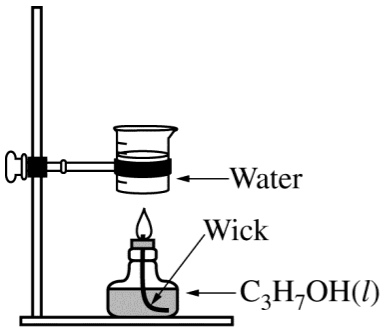
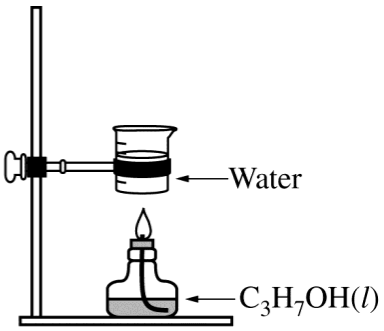
Question 5

$$2\ C_3H_7OH(l) + 9\ O_2(g) \rightarrow 6\ CO_2(g) + 8\ H_2O(g)$$

A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH(l)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $C_3H_7OH(l)$ that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH(l)$ combusted is determined by weighing the alcohol burner before and after combustion.



Initial



Final

Data from the experiment are given in the table below.

Mass of $C_3H_7OH(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	22.0°C
Final temperature of water	51.1°C
Specific heat of water	4.18 J/(g·°C)

(a) Calculate the magnitude of the heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)

$q = mc\Delta T$ $= (125.00\ g)(4.18\ J/(g\cdot°C))(51.1°C - 22.0°C)$ $= 15{,}200\ J = 15.2\ kJ$	1 point is earned for the correct calculation.

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Question 5 (continued)

(b) Based on the experimental data, if one mole of $C_3H_7OH(l)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.

$1\ \text{mol}\ C_3H_7OH \times \frac{60.09\ \text{g}\ C_3H_7OH}{1\ \text{mol}\ C_3H_7OH} \times \frac{15.2\ \text{kJ}}{0.55\ \text{g}\ C_3H_7OH} = 1661\ \text{kJ}$ $= 1.7 \times 10^3\ \text{kJ}$	1 point is earned for the correct amount of heat released. 1 point is earned for reporting the answer to the appropriate number of significant figures based on the experimental data.

(c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $C_3H_7OH(l)$ that is contaminated with water, which is miscible with $C_3H_7OH(l)$. The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

The final temperature measured by the second student would be less than that measured by the first student because: the actual mass of $C_3H_7OH(l)$ combusted will be less than 0.55 g OR combustion of the contaminated sample will also require vaporization of the water in the sample.	1 point is earned for the correct choice **with** a valid explanation.

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Question 6

Answer the following questions about $Mg(OH)_2$. At 25°C, the value of the solubility product constant, K_{sp}, for $Mg(OH)_2(s)$ is 1.8×10^{-11}.

(a) Calculate the number of grams of $Mg(OH)_2$ (molar mass 58.32 g/mol) that is dissolved in 100. mL of a saturated solution of $Mg(OH)_2$ at 25°C.

$1.8 \times 10^{-11} = [Mg^{2+}][OH^-]^2 = (x)(2x)^2 = 4x^3$ $x = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.65 \times 10^{-4}\ M = [Mg^{2+}] = [Mg(OH)_2]$ $0.100\ \text{L} \times \frac{1.65 \times 10^{-4}\ \text{mol}}{1\ \text{L}} \times \frac{58.32\ \text{g}\ Mg(OH)_2}{1\ \text{mol}\ Mg(OH)_2} = 9.6 \times 10^{-4}\ \text{g}\ Mg(OH)_2$	1 point is earned for calculating the solubility of $Mg(OH)_2$. 1 point is earned for calculating the correct mass based on the solubility of $Mg(OH)_2$.

(b) The energy required to separate the ions in the $Mg(OH)_2$ crystal lattice into individual $Mg^{2+}(g)$ and $OH^-(g)$ ions, as represented in the table below, is known as the lattice energy of $Mg(OH)_2(s)$. As shown in the table, the lattice energy of $Sr(OH)_2(s)$ is less than the lattice energy of $Mg(OH)_2(s)$. Explain why in terms of periodic properties and Coulomb's law.

Reaction	Lattice Energy (kJ/mol)
$Mg(OH)_2(s) \rightarrow Mg^{2+}(g) + 2\ OH^-(g)$	2900
$Sr(OH)_2(s) \rightarrow Sr^{2+}(g) + 2\ OH^-(g)$	2300

The Sr^{2+} ion is larger than the Mg^{2+} ion because it has additional occupied energy levels (or shells). Coulomb's law states that the force of attraction between cation and anion is inversely proportional to the square of the distance between them. Since the distance between Mg^{2+} and OH^- is shorter than the distance between Sr^{2+} and OH^-, the attractive forces in $Mg(OH)_2$ are stronger and, therefore, its lattice energy is greater.	1 point is earned for the correct comparison of cation sizes. 1 point is earned for indicating that smaller interionic distances lead to a greater lattice energy.

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Question 7

A student wants to determine the concentration of H_2O_2 in a solution of $H_2O_2(aq)$. The student can use one of two titrants, either dichromate ion, $Cr_2O_7^{2-}(aq)$, or cobalt(II) ion, $Co^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.

Dichromate as titrant: $Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) + 8\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ O_2(g) + 7\ H_2O(l)$

Cobalt(II) as titrant: $2\ Co^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Co^{3+}(aq) + 2\ H_2O(l)$

The half-reactions and the E° values for the systems related to the titrations above are given in the following table.

Half-Reaction	E° (V) at 298 K
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.84
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$	1.77
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.70

(a) Use the information in the table to calculate the following.

(i) E° for the reaction between $Cr_2O_7^{2-}(aq)$ and $H_2O_2(aq)$ at 298 K

$E^\circ = 1.33 - 0.70 = 0.63$ V	1 point is earned for correctly combining E° values.

(ii) E° for the reaction between $Co^{2+}(aq)$ and $H_2O_2(aq)$ at 298 K

$E^\circ = -1.84 + 1.77 = -0.07$ V	1 point is earned for correctly combining E° values.

2017 SCORING GUIDELINES

Question 7 (continued)

(b) Based on the calculated values of $E°$, the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

(i) Which titrant should the student choose? Explain your reasoning.

The student should use the dichromate ion for the titration because, for the reaction, the value of $E°$ is positive, which means that the reaction is thermodynamically favorable. OR $\Delta G° = -nFE°$ and n, F, and $E°$ are all positive numbers, therefore $\Delta G° < 0$, which means that the reaction is thermodynamically favorable.	1 point is earned for choosing the correct titrant **and** for understanding that a positive $E°$ or a negative $\Delta G°$ is required.

(ii) Calculate the value of $\Delta G°$, in kJ/mol_{rxn}, for the reaction between the chosen titrant and $H_2O_2(aq)$.

$\Delta G° = -nFE° = -6(96{,}485 \frac{C}{mol})(0.63 \frac{J}{C})(\frac{1\ kJ}{1000\ J}) = -360\ kJ/mol_{rxn}$	1 point is earned for calculating the value of $\Delta G°$.

AP® Chemistry
2016 Scoring Guidelines

SCORING GUIDELINES

Question 1

A student investigates the enthalpy of solution, ΔH_{soln}, for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of ± 0.1 g, and a thermometer with a precision of ± 0.1°C.

(a) To measure ΔH_{soln} for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl(*s*), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C.

(i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is 4.18 J/(g·°C). Include units with your answer.

$q = mc\Delta T = (110.0\text{ g})(4.18\text{ J/(g·°C)})(35.6\text{°C} - 15.0\text{°C})$ $= 9{,}470\text{ J} = 9.47\text{ kJ}$	1 point is earned for the correct setup. 1 point is earned for the correct answer with units.

(ii) Determine the value of ΔH_{soln} for LiCl in kJ/mol_{rxn}.

$10.0\text{ g LiCl} \times \frac{1\text{ mol LiCl}}{42.39\text{ g LiCl}} = 0.236\text{ mol LiCl}$ $\frac{-9.47\text{ kJ}}{0.236\text{ mol LiCl}} = -40.1\text{ kJ/mol}_{rxn}$	1 point is earned for the number of moles of LiCl. 1 point is earned for the correct ΔH_{soln} and the correct sign.

To explain why ΔH_{soln} for NaCl is different than that for LiCl, the student investigates factors that affect ΔH_{soln} and finds that ionic radius and lattice enthalpy (which can be defined as the ΔH associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

Ion	Ionic Radius (pm)
Li^+	76
Na^+	102

(b) Write the complete electron configuration for the Na^+ ion in the ground state.

$1s^2\,2s^2\,2p^6$	1 point is earned for the complete correct configuration.

SCORING GUIDELINES

Question 1 (continued)

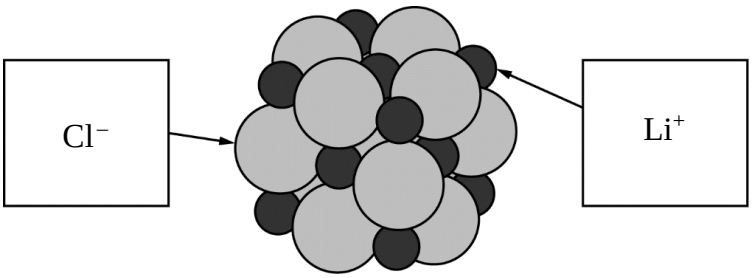
(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

The valence electrons in the Na^+ ion are in a higher principal energy level than the valence electrons in the Li^+ ion. Electrons in higher principal energy levels are, on average, farther from the nucleus.	1 point is earned for a correct explanation based on occupied principal energy levels.

(d) Which salt, LiCl or NaCl, has the greater lattice enthalpy? Justify your answer.

LiCl. Because the Li^+ ion is smaller than the Na^+ ion, the Coulombic attractions between ions in LiCl are stronger than in NaCl. This results in a greater lattice enthalpy.	1 point is earned for the correct choice and justification.

(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li^+ or Cl^-) in the boxes below.



See diagram above.	1 point is earned for both identifications.

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart. in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the exothermic dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

There are interactions between Li^+ ions and polar water molecules and between Cl^- ions and polar water molecules. These are ion-dipole interactions.	1 point is earned for identifying the particles that interact. 1 point is earned for correctly identifying the type of interaction.

2016 SCORING GUIDELINES

Question

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 *M* $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as reaction proceeds.

Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

It is an acid-base reaction. The weak acid $HC_2H_3O_2$ reacts with the weak base HCO_3^- with $HC_2H_3O_2$ donating a proton. It is an acid-base reaction. No solid precipitates, so it is not a precipitation reaction. None of the oxidation numbers change, so it is not a redox reaction.	1 point is earned for identifying the reaction as acid-base. 1 point is earned for the justification.

Based on the information above, identify the limiting reactant. Justify your answer with calculations.

$2.24 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.0 \text{ g}} = 0.0267 \text{ mol } NaHCO_3$ $60.0 \text{ mL} \times \frac{0.875 \text{ mol } HC_2H_3O_2}{1000 \text{ mL}} = 0.0525 \text{ mol } HC_2H_3O_2$ The $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$ react in a 1:1 ratio, so the limiting reactant is $NaHCO_3(s)$.	1 point is earned for calculating the number of moles of each reactant. 1 point is earned for identifying the limiting reactant consistent with the calculations.

The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

As the reaction proceeds, both reactants are consumed and their concentrations decrease. Collisions between reactant particles become less likely as their concentations decrease, thus the reaction rate slows.	1 point is earned for a valid explanation.

In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only Entropy only Both enthalpy and entropy

Entropy only should be circled.	1 point is earned for circling Entropy only.

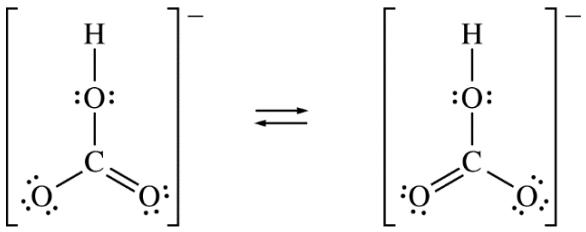
2016 SCORING GUIDELINES

Question 2 (continued)

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

Δ $= \Delta H° - T\Delta S°$ Reactions are thermodynamically favorable when $\Delta G°$ is negative. Since the reaction is endothermic (the flask gets cooler, $\Delta H°$ is positive), the reaction is not driven by enthalpy, because enthalpy does not help make $\Delta G°$ negative. Because there are no gases in the reactants and one of the products is a gas, $\Delta S°$ must be positive, which helps make $\Delta G°$ negative.	1 point is earned for a valid justification.

The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) HCO_3^- ion that is (are) consistent with the given information.



See diagram above.	1 point is earned for a correct Lewis structure of HCO_3^-. 1 point is earned for indicating resonance (e.g., two diagrams, or diagram with an arrow between the two appropriate oxygen atoms

A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 *M* $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.

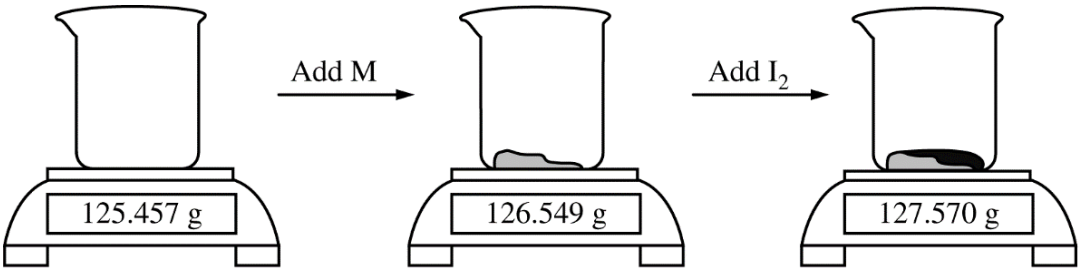
$C_2H_3O_2^- + H_3O^+ \rightarrow HC_2H_3O_2 + H_2O$ OR $C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$	1 point is earned for a correct equation.

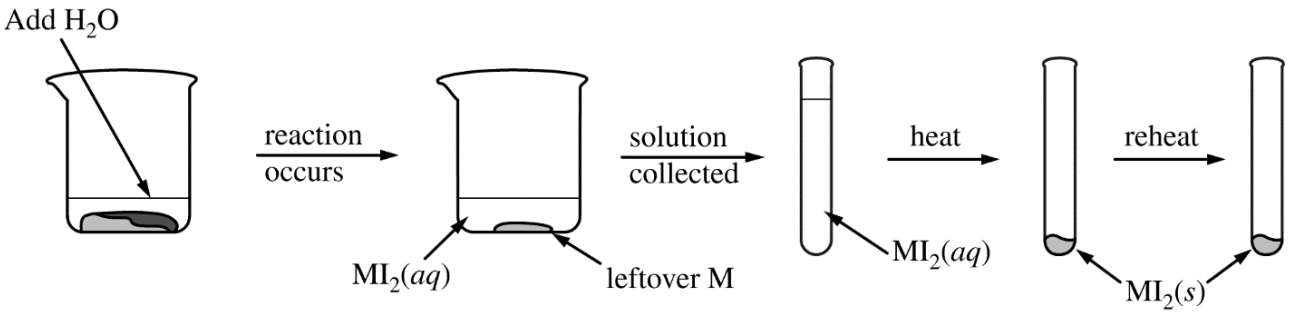
SCORING GUIDELINES

Question

$$M + I_2 \rightarrow MI_2$$

To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.





Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

SCORING GUIDELINES

Question 3 (continued)

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

$127.570 - 126.549 = 1.021 \text{ g } I_2$ $1.021 \text{ g } I_2 \times \frac{1 \text{ mol } I_2}{253.80 \text{ g } I_2} = 0.004023 \text{ mol } I_2$	1 point is earned for the number of moles.

(b) Calculate the molar mass of the unknown metal M.

Number of moles of I_2 = number of moles of M $1.284 \text{ g } MI_2 - 1.021 \text{ g } I_2 = 0.263 \text{ g M}$ Molar mass of M = $\frac{0.263 \text{ g M}}{0.004023 \text{ mol M}} = 65.4 \text{ g/mol}$	1 point is earned for the number of grams of M. 1 point is earned for the molar mass.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student could dissolve the compound in water or melt the compound and see if the solution/melt conducts electricity. If the solution/melt conducts electricity, mobile ions capable of carrying charge must be present, thus the compound is likely to be ionic. OR The student could heat the compound until it melts or boils. If the melting/boiling point is very high, then the compound is likely to be ionic.	1 point is earned for an appropriate test. 1 point is earned for explaining how the results would support the hypothesis.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

SCORING GUIDELINES

Question 3 (continued)

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

Both Br_2 and I_2 molecules are nonpolar molecules, therefore the only possible intermolecular forces are London dispersion forces. The London dispersion forces are stronger in I_2 because it is larger in size with more electrons and/or a more polarizable electron cloud. The stronger London dispersion forces in I_2 result in a higher melting point,which makes I_2 a solid at room temperature.	1 point is earned for identifying the forces in each substance as London dispersion forces. 1 point is earned for explaining why the forces are stronger in I_2 than in Br_2.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half-reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\ e^- \rightarrow 2\ S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)$	0.54
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer and include a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $Na_2S_2O_3(aq)$ $Na_2S_4O_6(aq)$

[$Na_2S_2O_3(aq)$ should be circled.] The reaction between $S_2O_3^{2-}(aq)$ and $I_2(s)$ will be thermodynamically favorable because $E°$ for the reaction is positive ($E° = 0.54 - 0.08 = +0.46$ V), from which it follows that $\Delta G°$ is negative because $\Delta G° = -nFE°$.	1 point is earned for the correct choice. 1 point is earned for a correct justification.

(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$	1 point is earned for the correct equation.

SCORING GUIDELINES

Question

$$C_6H_5OH(aq) + H_2O(l) \rightleftarrows C_6H_5O^-(aq) + H_3O^+(aq) \qquad K_a = 1.12 \times 10^{-10}$$

Phenol is a weak acid that partially dissociates in water, according to the equation above.

(a) What is the pH of a 0.75 *M* $C_6H_5OH(aq)$ solution?

$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$ $1.12 \times 10^{-10} = \frac{x^2}{(0.75 - x)}$ Assume that $x << 0.75$. $x^2 = 8.4 \times 10^{-11}$ $x = \sqrt{8.4 \times 10^{-11}}$ $x = 9.2 \times 10^{-6}\ M$ $pH = -\log[H^+] = -\log(9.2 \times 10^{-6}) = 5.04$	1 point is earned for a correct setup and calculation of $[H^+]$. 1 point is earned for the correct setup and calculation of pH based on a correct setup for the $[H^+]$ calculation.

(b) For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle <u>each</u> pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

Numbers 10 through 14 should be circled. When pH > pK_a , the deprotonated form will predominate. pK_a = –log(1.12×10^{-10}) = 9.95, therefore at pH 10 and above, $[C_6H_5O^-] > [C_6H_5OH]$.	1 point is earned for circling 10–14. 1 point is earned for the justification.

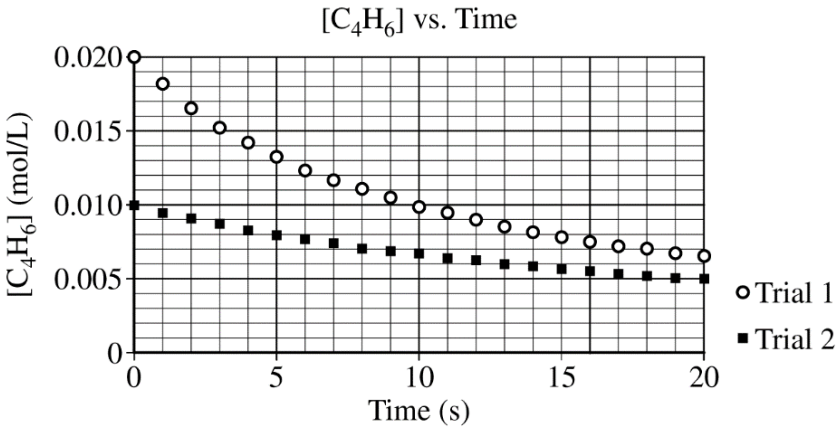
1 2 3 4 5 6 7 8 9 10 11 12 13 14

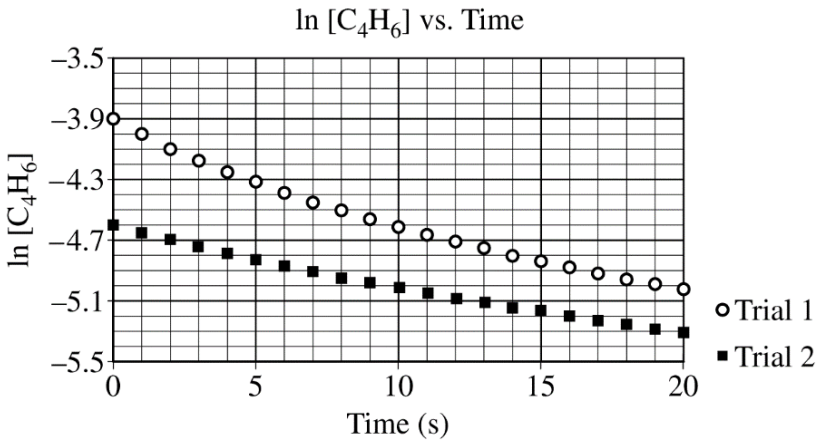
SCORING GUIDELINES

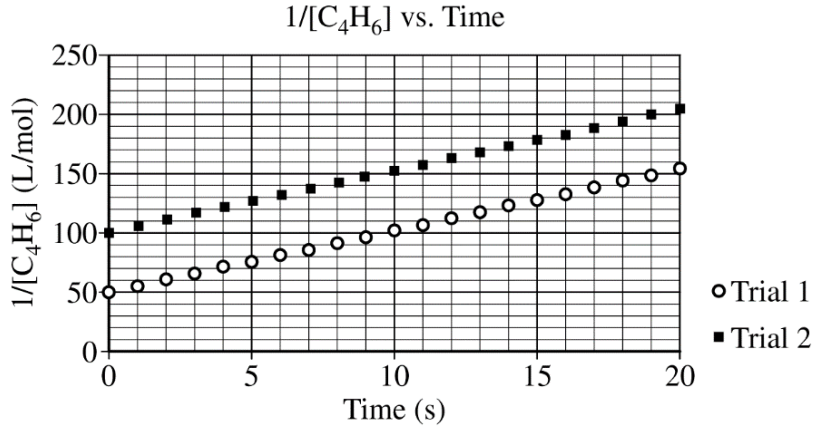
Question

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.







SCORING GUIDELINES

Question 5 (continued)

(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

For trial 1, $\frac{n}{V} = 0.020$ mol/L (or assume the volume of the vessel is 1.0 L; the number of moles of C_4H_6 in the vessel would then be 0.020 mol). $PV = nRT$ $P = \frac{nRT}{V} = \frac{(0.020 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(625 \text{ K})}{1.0 \text{ L}} = 1.0$ atm	1 point is earned for a correct setup. 1 point is earned for the correct answer.

(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

Second order (because the plot of $1/[C_4H_6]$ is a straight line).	1 point is earned for the correct order.

(c) The initial rate of the reaction in trial 1 is 0.0010 mol/(L·s). Calculate the rate constant, k, for the reaction at 625 K.

From the second-order rate law (differential form): rate = $k[C_4H_6]^2$ $\Rightarrow k = \frac{\text{rate}}{([C_4H_6])^2} = \frac{0.0010 \text{ mol/(L·s)}}{(0.020 \text{ mol/L})^2} = 2.5$ L/(mol·s) OR From the second-order rate law (integrated form): $\frac{1}{[C_4H_6]_t} = 2kt + \frac{1}{[C_4H_6]_0}$ The coefficient of t is equal to $2k$ because of the reaction stoichiometry. The slope of the line in the plot of $\frac{1}{[C_4H_6]}$ versus time is $2k$. Thus slope = 5.0 L/(mol·s) = $2k$, therefore $k = 2.5$ L/(mol·s). Note: Students who choose the second method of determining k but omit the factor of 2, thereby getting an answer of 5.0 L/(mol·s), still earn the point.	1 point is earned for the correct value.

SCORING GUIDELINES

Question

$$Ba^{2+}(aq) + EDTA^{4-}(aq) \rightleftarrows Ba(EDTA)^{2-}(aq) \qquad K = 7.7 \times 10^{7}$$

The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as $EDTA^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of $EDTA^{4-}$ with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $EDTA^{4-}(aq)$ concentration of 0.30 *M* is mixed with 50.0 mL of 0.20 *M* $Ba(NO_3)_2$ to produce 100.0 mL of solution.

(a) Considering the value of K for the reaction, determine the concentration of $Ba(EDTA)^{2-}(aq)$ in the 100.0 mL of solution. Justify your answer.

Based on the *K* value, the reaction goes essentially to completion. $Ba^{2+}(aq)$ is the limiting reactant. The concentration of Ba^{2+} when the solutions are first mixed but before any reaction takes place is 0.20 *M*/2 = 0.10 *M*. Thus the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is 0.10 *M*.	1 point is earned for indicating that the equilibrium concentration of $Ba(EDTA)^{2-}(aq)$ is the same as the original concentration of Ba^{2+} when the solutions are mixed. 1 point is earned for the concentration with appropriate calculations.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $Ba^{2+}(aq)$ present in the solution greater than, less than, or equal to the number of moles of $Ba^{2+}(aq)$ present in the original solution before it was diluted? Justify your answer.

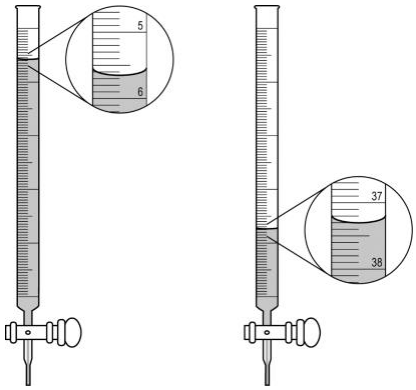
The number of moles of $Ba^{2+}(aq)$ increases because the percent dissociation of $Ba(EDTA)^{2-}(aq)$ increases as the solution is diluted. OR A mathematical justification such as the following: The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original values. Immediately after the dilution, the reaction quotient, Q, can be determined as shown below. $$Q = \frac{\frac{1}{10}[Ba(EDTA)^{2-}]}{\frac{1}{10}[Ba^{2+}] \times \frac{1}{10}[EDTA^{4-}]} = 10K$$ Because $Q > K$, the net reaction will produce more reactants to move toward equilibrium, so the number of moles of $Ba^{2+}(aq)$ will be greater than the number in the original solution.	1 point is earned for stating that the number of moles of $Ba^{2+}(aq)$ will increase. 1 point is earned for a valid justification.

SCORING GUIDELINES

estion

A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 *M* NaOH(*aq*), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

(a) The images below show the buret before the titration begins (below left) and at the end point (below right). What should the student record as the volume of NaOH(*aq*) delivered to the flask?



37.30 mL – 5.65 mL = 31.65 mL	1 point is earned for the correct volume.

(b) Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.

At the equivalence point, moles OH^- added = moles of H^+ consumed. Because HA is monoprotic: $(0.110\ M)(0.03165\ \text{L}) \times \frac{1\ \text{mol HA}}{1\ \text{mol NaOH}} \times \frac{1}{0.0250\ \text{L}} = 0.139\ M$ OR moles of H^+ consumed = $M_a V_a$ $M_a V_a = M_b V_b$ Therefore, $M_a = \frac{M_b V_b}{V_a} = \frac{(0.110\ M)(0.03165\ \text{L})}{0.0250\ \text{L}} = 0.139\ M$	1 point is earned for the correct setup and molarity.

(c) In a second trial, the student accidentally added more NaOH(*aq*) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculated acid concentration for the second trial? Justify your answer.

The error would increase the calculated acid concentration. A volume of NaOH(*aq*) larger than the actual volume needed to reach the equivalence point, would lead to a calculation of moles of base that would be greater than the moles of acid actually present in the solution. The assumption that the moles of acid are the same as the moles of base would lead to a calculated concentration of acid that would be higher than the actual concentration.	1 point is earned for indicating an increase. 1 point is earned for a valid justification.