AP® Chemistry
2016 Scoring Guidelines

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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.

$q = mc\Delta T = (110.0\text{ g})(4.18\text{ J/(g}\cdot°\text{C))}(35.6°\text{C} - 15.0°\text{C})$ $= 9{,}470\text{ J} = 9.47\text{ kJ}$	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} <u>and</u> 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.

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Question 1 (continued)

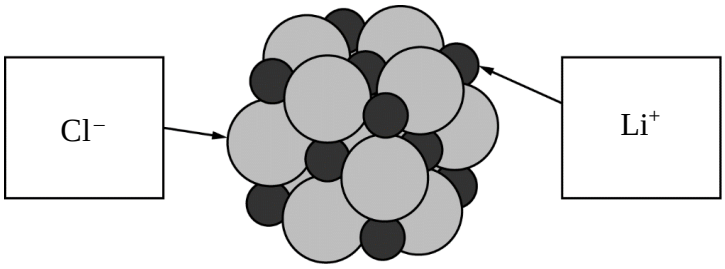
(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

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.

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Question 2

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

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 the reaction proceeds.

(a) 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. OR 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.

(b) 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.

(c) 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.

(d) 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.

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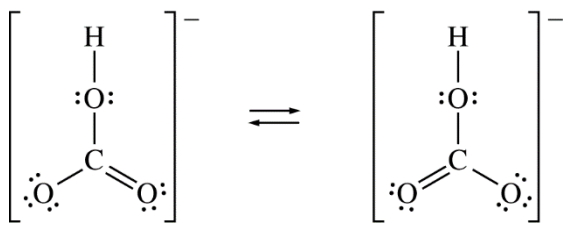
Question 2 (continued)

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

$\Delta G° = \Delta H° - T\Delta S°$ 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.

(e) 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) for the 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 one diagram with an arrow between the two appropriate oxygen atoms).

(f) 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 4.7.

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

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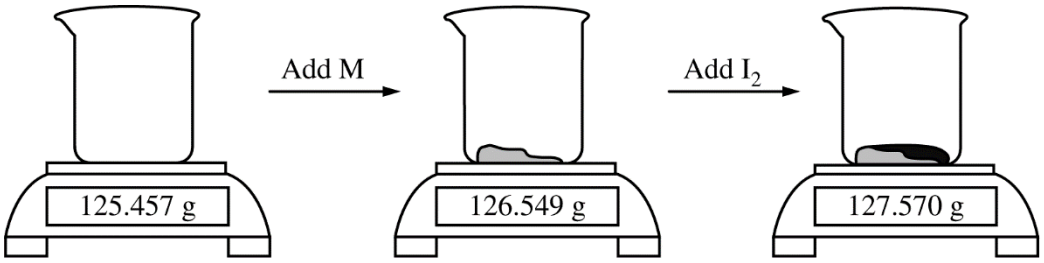
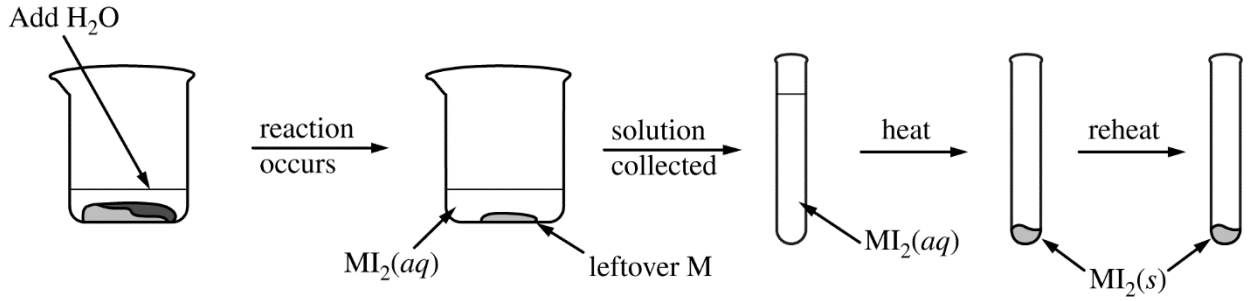
Question 3

$$M + I_2 \rightarrow MI_2$$

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

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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.

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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.

$H_2O_2(aq)$ $\qquad$ $Na_2S_2O_3(aq)$ $\qquad$ $Na_2S_4O_6(aq)$

[$Na_2S_2O_3(aq)$ 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.

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Question 4

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

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?

$K_a = \dfrac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$ $1.12 \times 10^{-10} = \dfrac{x^2}{(0.75 - x)}$ 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. p$K_a = -\log(1.12 \times 10^{-10}) = 9.95$, 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

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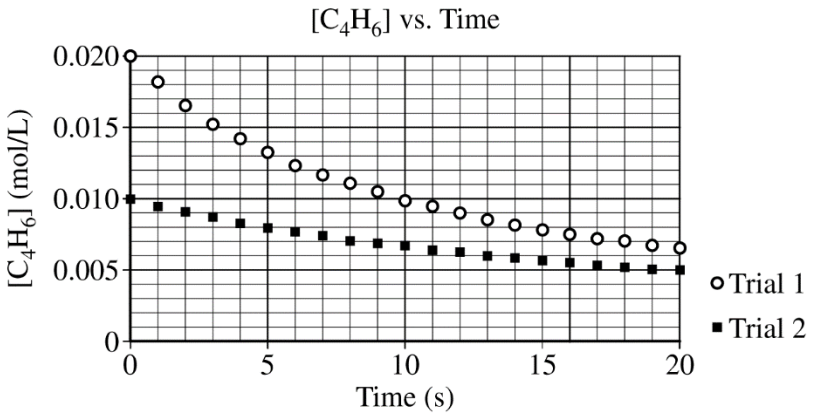
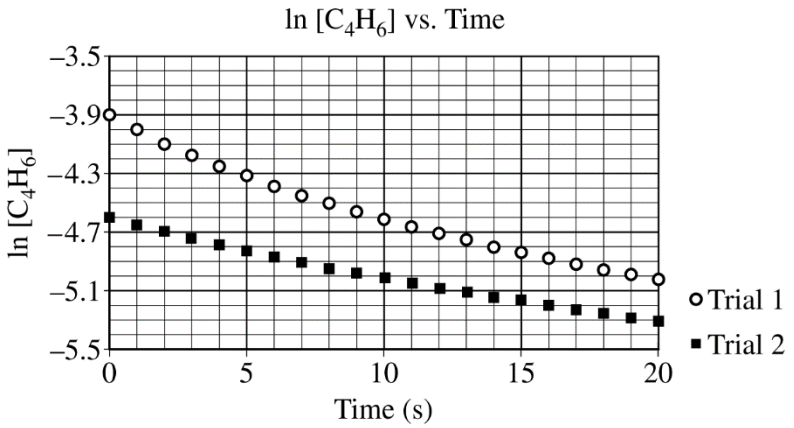
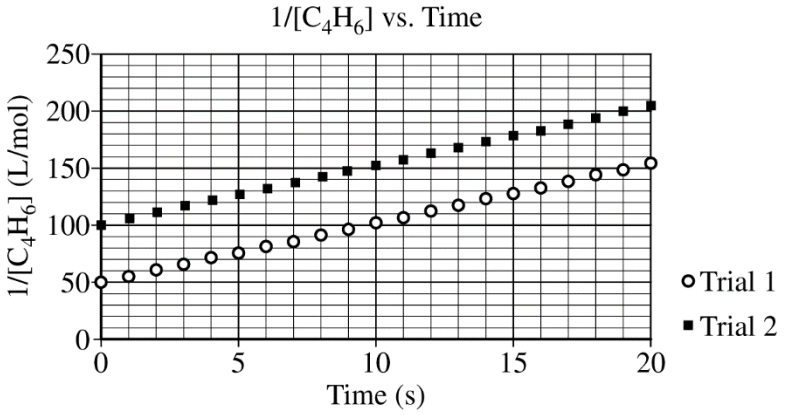
Question 5

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

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.







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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). $PV = nRT$ $P = \frac{nRT}{V} = \frac{(0.020\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(625\text{ K})}{1.0\text{ L}} = 1.0\text{ atm}$	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 = $k[C_4H_6]^2$ $\Rightarrow k = \frac{\text{rate}}{([C_4H_6])^2} = \frac{0.0010\text{ mol/(L·s)}}{(0.020\text{ mol/L})^2} = 2.5\text{ L/(mol·s)}$ 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). <u>Note:</u> 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.

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Question 6

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

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.

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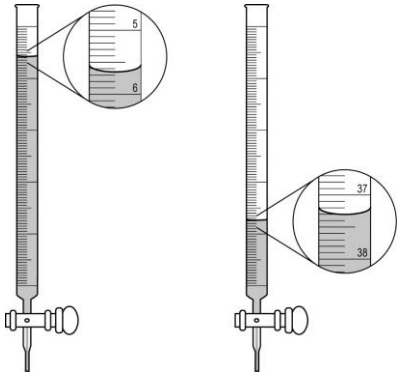
Question 7

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.

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