Question 2: Long Answer — 10 points

A (i) For the correct calculated value: **Point 01**

$$2.883 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.1600 \text{ mol } H_2O$$

(ii) For the correct calculated number of moles of H (may be implicit): **Point 02**

$$0.1600 \text{ mol } H_2O \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.3200 \text{ mol H}$$

For the correct empirical formula. **Point 03**

Examples of acceptable responses may include the following:

- $x : y : z$ = (moles of C):(moles of H):(moles of O)
  $x : y : z = 0.2400 : 0.3200 : 0.2400 = 3 : 4 : 3$
  Therefore, the empirical formula of ascorbic acid is $C_3H_4O_3$.
- $0.2400 \text{ mol } CO_2 \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.2400 \text{ mol C}$
  $\frac{0.3200 \text{ mol H}}{0.2400 \text{ mol C}} = \frac{4 \text{ H}}{3 \text{ C}}$
  Given that the ratio of C:O *is* 1:1, *the empirical formula of ascorbic acid is* $C_3H_4O_3$.

B (i) For the correct calculated value: **Point 04**

$$0.0160 \text{ L NaOH} \times \frac{0.0550 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol HAsc}}{1 \text{ mol NaOH}} = 8.80 \times 10^{-4} \text{ mol HAsc}$$

$$\frac{8.80 \times 10^{-4} \text{ mol HAsc}}{0.0100 \text{ L}} = 0.0880 \ M \text{ HAsc}$$

(ii) For the correct pK_a: **Point 05**

4.1 (*acceptable range:* 4.0 – 4.3)

(iii) For the correct ratio, consistent with part B (ii): **Point 06**

Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[Asc^-]}{[HAsc]}\right)$$

$$4.7 = 4.1 + \log\left(\frac{[Asc^-]}{[HAsc]}\right)$$

$$\frac{[Asc^-]}{[HAsc]} = 10^{0.6} = 4.0$$

C (i) For a correct explanation. **Point 07**

Examples of acceptable responses may include the following:

- $\frac{4.914 \times 10^{-4}}{2.457 \times 10^{-4}} = \left(\frac{0.900}{0.450}\right)^a$, thus $a = 1$
- *Comparing trials 1 and 3, the rate doubles when the concentration of ascorbic acid is doubled and the triiodide ion concentration is constant, indicating that the process is first order with respect to ascorbic acid.*

(ii) For the correct calculated value: **Point 08**

$rate = k[HAsc][I_3^-]$

Using trial 1 data:

$$k = \frac{rate}{[HAsc][I_3^-]} = \frac{2.457 \times 10^{-4} \ M/s}{(0.450 \ M)(1.200 \ M)} = 4.55 \times 10^{-4} M^{-1} \text{ s}^{-1}$$

For the correct units: **Point 09**

M^{-1} s^{-1}

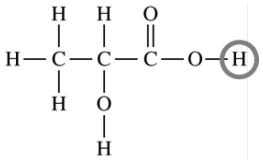
D For the correct answer: **Point 10**

Ion-dipole attractions are present between I_3^- *ions and water but not between* I_2 *molecules and water.*

Question 1: Long Answer — 10 points

(a) For the correct circled atom: **1 point**

The rightmost hydrogen atom should be circled.



(b) For the correct calculated value: **1 point**

$$\frac{(10.22\text{ g})\left(\frac{1\text{ mol}}{40.00\text{ g}}\right)}{0.500\text{ L}} = 0.511\ M$$

(c) For the correct pK_a: **1 point**

3.9 *(acceptable range: 3.7 – 4.0)*

(d) (i) For the X at the correct point: **1 point**

The X should be at a point greater than or equal to 3 mL *and less than* 8 mL.

(ii) For a correct justification: **1 point**

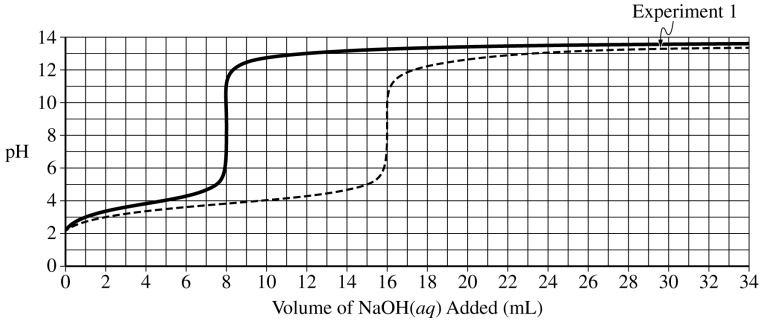
More acid particles are present than conjugate base particles, meaning that the titration is before the half-equivalence point.

(iii) For a curve showing the correct equivalence point: **1 point**

The equivalence point should be at 8 mL. *See example response below.*

For a curve with appropriate initial and final pH with a correct shape: **1 point**

The drawn curve should begin at the same pH, *gradually increase, rise sharply at a volume different than* 16 mL, *and end at a* pH *similar to the first curve.*



Total for part (d) 4 points

(e) (i) For the correct calculated value: **1 point**

$q = mc\Delta T = (200.0\text{ g})(4.2\text{ J/(g}\cdot\text{°C)})(23.2\text{°C} - 20.0\text{°C}) = 2700\text{ J}$

(ii) For the correct calculated value: **1 point**

$q_{rxn} = -q_{soln} = -2700\text{ J} = -2.7\text{ kJ}$

$$\Delta H_{rxn} = \frac{q_{rxn}}{\text{mol}} = \frac{-2.7\text{ kJ}}{(0.100\text{ L})(0.500\text{ mol/L})} = -54\text{ kJ/mol}_{rxn}$$

(iii) For the correct answer and a valid justification: **1 point**

Agree. The heat lost from the system would result in a lower final temperature, which results in values of ΔT, q_{soln}, *and* ΔH *that are smaller than the actual value.*

Total for part (e) 3 points

Total for question 1 10 points

Question 2: Long Answer — 10 points

(a) (i) For the correct calculated value: **1 point**

$$0.0114 \text{ mol } CO_2 \times \frac{44.01 \text{ g}}{1 \text{ mol}} = 0.502 \text{ g } CO_2$$

(ii) For the correct calculated value: **1 point**

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(0.0114 \text{ mol})(0.08206 \ \frac{\text{L·atm}}{\text{mol·K}})(293 \text{ K})}{1.25 \text{ atm}} = 0.219 \text{ L}$$

Total for part (a) **2 points**

(b) (i) For a correct claim: **1 point**

The surface area of the solid reactants increases.

(ii) For the correct answer and a valid justification: **1 point**

Shorter than. The powdered solids have a larger surface area than the solid chunks, thus collisions between water and the surface particles occur more frequently, resulting in a faster rate of dissolution and a shorter amount of time to dissolve the solids.

(iii) For the correct answer and a valid justification: **1 point**

Equal to. Both experiments begin with the same amount of reactants, so they will produce the same number of moles of $CO_2(g)$ *under the same conditions of pressure and temperature; therefore, the final volume will be the same.*

Total for part (b) **3 points**

(c) For the correct answer and a valid justification: **1 point**

Accept one of the following:

- $NaHCO_3$ *is the limiting reactant because changing the mass of* $NaHCO_3$ *alters the amount of* CO_2 *produced.*
- $NaHCO_3$ *is the limiting reactant because the amount present has a smaller theoretical yield of the* CO_2 *product.*

$$1.543 \text{ g } H_2C_4H_2O_4 \times \frac{1 \text{ mol } H_2C_4H_2O_4}{116.07 \text{ g}} \times \frac{2 \text{ mol } CO_2}{1 \text{ mol } H_2C_4H_2O_4} = 0.02659 \text{ mol } CO_2$$

$$1.251 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.01 \text{ g}} \times \frac{2 \text{ mol } CO_2}{2 \text{ mol } NaHCO_3} = 0.01489 \text{ mol } CO_2$$

(d) For a valid explanation: **1 point**

The entropy change is positive because the aqueous reactants produce 2 moles of gas particles, according to the balanced chemical equation. Gases are far more dispersed (occupy a greater number of microstates) than condensed phases, so the entropy of the products is greater than that of the reactants.

(e) For the correct answer and a valid justification: **1 point**

Accept one of the following:

- *Disagree. The reaction is endothermic and has a positive entropy change. Thus, the reaction is only thermodynamically favorable at a high enough temperature such that the magnitude of* $-T\Delta S$ *is greater than that of* ΔH.
- *Disagree. For the reaction to be thermodynamically favorable* $(\Delta G < 0)$ *at all temperatures, the reaction must be exothermic* $(\Delta H < 0)$ *and have a positive entropy change* $(\Delta S > 0)$.

(f) For the correct calculated value: **1 point**

$$pK_{a_2} = -\log\left(8.5 \times 10^{-7}\right) = 6.07$$

(g) For the correct calculated value: **1 point**

$$\text{pH} = pK_{a_2} + \log\frac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^{-}]}$$

$$\frac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^{-}]} = 10^{(\text{pH}-pK_{a_2})} = 10^{(7.00-6.07)} = 8.5$$

Total for question 2 **10 points**

Question 1: Long Answer — 10 points

(a) For the correct calculated value: **1 point**

$$0.300\text{ g } C_8H_8O_3 \times \frac{1\text{ mol } C_8H_8O_3}{152.15\text{ g}} \times \frac{1\text{ mol } HC_7H_5O_3}{1\text{ mol } C_8H_8O_3} \times \frac{138.12\text{ g}}{1\text{ mol } HC_7H_5O_3} = 0.272\text{ g } HC_7H_5O_3$$

(b) For the correct answer and a valid justification: **1 point**

Yes (consistent). Because the acid is soluble in water, some crystals may dissolve during rinsing, causing the mass of the collected precipitate to be lower than expected. This would lead to a percent yield less than 100%.

(c) For the correct calculated value of either q: **1 point**

Accept one of the following:

- $q_{heat} = mc\Delta T = (0.105\text{ g})(1.17\text{ J/(g} \cdot \text{°C)})(159\text{°C} - 25\text{°C}) = 16.5\text{ J}$
- $q_{melt} = 0.105\text{ g} \times \frac{1\text{ mol}}{138.12\text{ g}} \times \frac{27{,}100\text{ J}}{1\text{ mol}} = 20.6\text{ J}$

For the correct calculated value of the other q and the total heat: **1 point**

$q_{total} = q_{heat} + q_{melt} = 16.5\text{ J} + 20.6\text{ J} = 37.1\text{ J}$

Total for part (c) 2 points

(d) For a correct explanation: **1 point**

Molecules of salicylic acid have more hydrogen bonding sites than molecules of methyl salicylate have, which leads to stronger intermolecular forces and a higher melting point for salicylic acid.

(e) For the correct answer: **1 point**

The pK_a *is approximately 3.*

(f) For the correct answer and a valid justification, consistent with part (e): **1 point**

Accept one of the following:

- *The conjugate base,* $C_7H_5O_3^-$. *When* pH = 4, *the titration is beyond the half-equivalence point, where* $[HC_7H_5O_3] = [C_7H_5O_3^-]$. *Thus,* $[C_7H_5O_3^-]$ *must be greater than* $[HC_7H_5O_3]$.
- *The conjugate base,* $C_7H_5O_3^-$. *Because the* pH *of the solution is greater than the* pK_a *of the acid, the majority of the molecules will be deprotonated.*

(g) For the correct calculated value: **1 point**

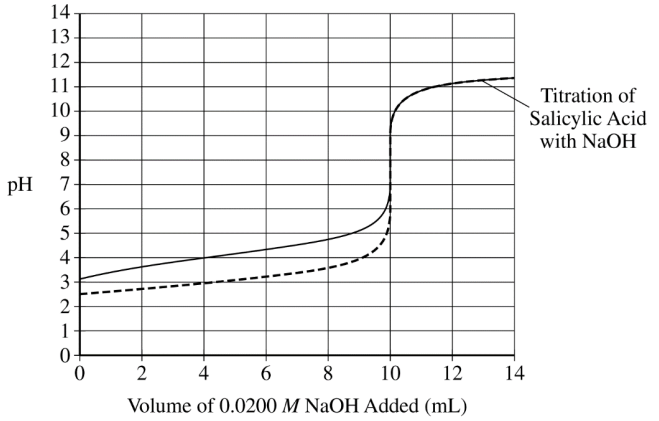
$pK_a = -\log(6.3 \times 10^{-5}) = 4.20$

(h) For a curve that shows a correct starting and half-equivalence point, consistent with part (g): **1 point**

The curve starts at pH ≈ 3.11 *and passes through the* pK_a *calculated in part (g) at* 5 *mL*.
See example response below.

For a curve that shows the correct equivalence point: **1 point**

The curve inflects vertically at 10 *mL showing the same volume of base needed to reach the equivalence point.*



Total for part (h) 2 points

Total for question 1 10 points

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Scoring Guidelines

2018 SCORING GUIDELINES

Question 1

$$Na_2S_2O_3(aq) + 4\ NaOCl(aq) + 2\ NaOH(aq) \rightarrow 2\ Na_2SO_4(aq) + 4\ NaCl(aq) + H_2O(l)$$

A student performs an experiment to determine the value of the enthalpy change, ΔH°_{rxn}, for the oxidation-reduction reaction represented by the balanced equation above.

Determine the oxidation number of Cl in NaOCl.

+1	1 point is earned for the correct answer.

Calculate the number of grams of $Na_2S_2O_3$ needed to prepare 100.00 mL of 0.500 *M* $Na_2S_2O_3$(

$100.00\ mL \times \frac{0.500\ mol\ Na_2S_2O_3}{1000\ mL} \times \frac{158.10\ g\ Na_2S_2O_3}{1\ mol\ Na_2S_2O_3}$ $= 7.90\ g\ Na_2S_2O_3$	1 point is earned for the correct number of moles of $Na_2S_2O_3$ (may be implicit). 1 point is earned for the correct calculation of mass of Na_2S_2 consistent with the number of moles.

In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (*M*)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5.00
NaOCl(*aq*)	0.500	5.00
NaOH(*aq*)	0.500	5.00

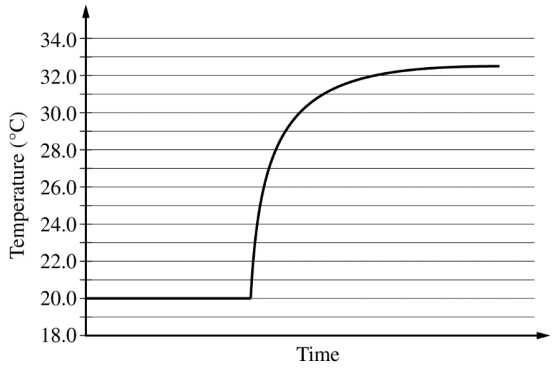
Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

NaOCl is the limiting reactant. Given that equal numbers of moles of each reactant were present initially, it follows from the coefficients of the reactants in the balanced equation that NaOCl will be depleted first.	1 point is earned for identifying limiting reactant and providing a valid justification.

2018 SCORING GUIDELINES

Question 1 (continued)

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



According to the graph, what is the temperature change of the reaction mixture?

From the graph the final temperature is 32.5°C. $\Delta = T_f - T_i = 32.5°C - 20.0°C = 12.5°C$	1 point is earned for the correct value Δ

The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

$= mc\Delta T$ $= (15.21\ g)(3.94\ J/(g·°C))(12.5°C) = 749\ J$	1 point is earned for the correct calculation q consistent with the ΔT value from part (

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, ΔH°_{rxn}, in kJ/mol$_{rxn}$. Include the appropriate algebraic sign with your answer.

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Question 1 (continued)

$_{aOCl} = 5.00\ \text{mL} \times \frac{0.500\ \text{mol NaOCl}}{1000\ \text{mL NaOCl}} = 0.00250\ \text{mol NaOCl}$ $= 0.00250\ \text{mol NaOCl} \times \frac{1\ \text{mol}_{rxn}}{4\ \text{mol NaOCl}} = 0.000625\ \text{mol}_{rxn}$ $\Delta H^\circ_{rxn} = \frac{-0.749\ \text{kJ}}{0.000625\ \text{mol}_{rxn}} = -1.20 \times 10^3\ \text{kJ/mol}_{rxn}$	1 point is earned for correctly calculating the value of mol consistent with the limiting reactant in part 1 point is earned for a negative ΔH°_{rxn} obtained by dividing the calculated value of q by the calculated value of mol

e student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	10.0
$NaOCl(aq)$	0.500	10.0
$NaOH(aq)$	0.500	10.0

The magnitude of the enthalpy change, ΔH°_{rxn}, in kJ/mol_{rxn}, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

By doubling the volumes, the number of moles of the reactants are doubled, which doubles the amount of energy produced. Therefore ıe amount of heat per mole will remain the same. OR In the second experiment, $\Delta H^\circ_{rxn} = \frac{2mc\Delta T}{2n} = \frac{mc\Delta T}{n} = \Delta H^\circ_{rxn}$. Thus the magnitude is the same as calculated in the first experiment.	1 point is earned for valid explanation.

Write the balanced net ionic equation for the given reaction.

$)_3^{2-}(aq) + 4\ OCl^-(aq) + 2\ OH^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + 4\ Cl^-(aq) + H_2O(l)$	1 point is earned for the correct net ionic equation.

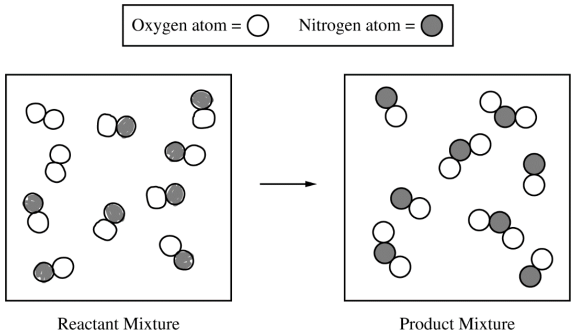
2018 SCORING GUIDELINES

Question 2

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

(The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $NO(g)$ and O_2 would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



See sample student response above. (8 molecules of NO and 2 molecules of O_2)	1 point is earned for correctly representing molecules of NO and O 1 point is earned for correctly representing atom conservation.

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
$-40.4\ \text{kJ/mol}_{rxn}$	$-138.5\ \text{J/(K·mol}_{rxn})$	$0.87\ \text{kJ/mol}_{rxn}$

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Question 2 (continued)

The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

(i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

$^{\circ} = -RT\ln K$ $K = e^{-\Delta G^{\circ}/RT}$ $K = e^{-\frac{870\ \text{J/mol}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}}$ $K = 0.70$	1 point is earned for a correct calculation of K.

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

No, the pressure will not equal 1.0 atm. $P_{N_2O_3}$ would only equal 1.0 atm if the reaction goes to completion. The value of K indicates that a substantial amount of reactants will be present at equilibrium.	1 point is earned for a correct choice and valid justification based on the value of

The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

Disagree. Because the reaction is exothermic, increasing the temperature of the reaction will favor the formation of the reactants (according to Le Chatelier's principle).	1 point is earned for the correct choice and a correct justification.

g) reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

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Question 2 (continued)

The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

See sample response above. (Line segments can be used to represent electron pairs.)	1 point is earned for a valid diagram.

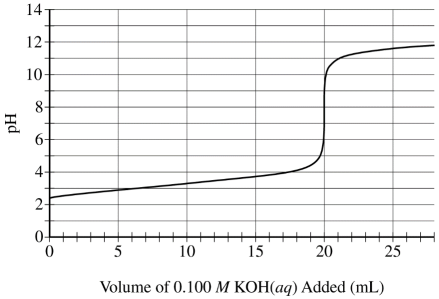
(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

sp^2	1 point is earned for the correct answer.

To produce an aqueous solution of HNO_2, the student bubbles $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 $KOH(aq)$. The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The following titration curve shows the change in pH of the solution during the titration.



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Question 2 (continued)

Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

$\text{mL KOH} \times \frac{0.100 \text{ mol KOH}}{1000 \text{ mL KOH}} = 0.0020 \text{ mol KOH added}$ $\Rightarrow$ 0.0020 mol HNO_2 in 100. mL of solution because the stoichiometry of the neutralization reaction is 1 to 1. $\frac{0.0020 \text{ mol } HNO_2}{0.100 \text{ L}} = 0.020\ M\ HNO_2$	1 point is earned for the correct calculation of the initial concentration.

(ii) estimate the value of pK_a for $HNO_2(aq)$

The value of pK_a is about 3.4.	1 point is earned for an acceptable estimate for the value of pK_a.

During the titration, after a volume of 15 mL of 0.100 M KOH(aq) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

(aq) The titration is past the half-equivalence point; therefore, there will be more conjugate base present than acid.	1 point is earned for the correct choice and a valid justification.

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Question 3

Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+}.

Write the ground-state electron configuration of the Fe^{2+} ion.

^{2} $2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ OR [Ar] $3d^6$	1 point is earned for a correct electron configuration.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

Both ions have the same nuclear charge; however, the greater number of electrons in the outermost shell of Fe^{2+} results in greater electron-electron repulsion within that shell, leading to a larger radius.	1 point is earned for a valid explanation.

Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

Coulomb's law: $F \propto \frac{q_1\ q_2}{r^2}$ (need not be explicitly stated) In comparison to the Fe^{2+} ion, the Fe^{3+} ion has a higher charge. The smaller size of Fe^{3+} allows it to get closer to a water molecule.	1 point is earned for a valid explanation.

A student obtains a solution that contains an unknown concentration of $Fe^{2+}(aq)$. To determine the concentration of $Fe^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $MnO_4^-($ which converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

Write the balanced equation for the half-reaction for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$.

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	1 point is earned for the correct half-reaction.

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Question 3 (continued)

The student titrates a 10.0 mL sample of the $Fe^{2+}(aq)$ solution. Calculate the value of $[Fe^{2+}]$ in solution if it takes 17.48 mL of added 0.0350 *M* $KMnO_4(aq)$ to reach the equivalence point of the titration.

$17.48 \text{ mL} \times \frac{0.0350 \text{ mol } KMnO_4}{1000 \text{ mL}} = 0.000612 \text{ mol } KMnO_4$ $0.000612 \text{ mol } KMnO_4 \times \frac{5 \text{ mol } Fe^{2+}}{1 \text{ mol } KMnO_4} = 0.003059 \text{ mol } Fe^{2+}$ $\frac{0.003059 \text{ mol } Fe^{2+}}{0.0100 \text{ L}} = 0.306 \, M \, Fe^{2+}$	1 point is earned for calculating the number of moles of $KMnO_4$ (may be implicit). 1 point is earned for the correct concentration of Fe^{2+}(

To deliver the 10.0 mL sample of the $Fe^{2+}(aq)$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL beaker
- 25 mL graduated cylinder
- 25 mL volumetric flask

Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $Fe^{2+}(aq)$ solution.

The volumetric flask is designed to contain only 25.00 mL precisely.	1 point is earned for a valid explanation.

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Question 3 (continued)

In a separate experiment, the student is given a sample of powdered Fe(*s*) that contains an inert impurity. The student uses a procedure to oxidize the Fe(*s*) in the sample to $Fe_2O_3(s)$. The student collects the following data during the experiment.

Mass of Fe(*s*) with inert impurity	6.724 g
Mass of $Fe_2O_3(s)$ produced	7.531 g

Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

$7.531 \text{ g } Fe_2O_3 \times \frac{1 \text{ mol } Fe_2O_3}{159.70 \text{ g } Fe_2O_3} = 0.04716 \text{ mol } Fe_2O_3$ $0.04716 \text{ mol } Fe_2O_3 \times \frac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3} = 0.09431 \text{ mol Fe}$	1 point is earned for correct calculation.

Calculate the percent by mass of Fe in the original sample of powdered Fe(*s*) with the inert impurity.

$0.09431 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol}} = 5.267 \text{ g Fe}$ $\frac{5.267 \text{ g Fe}}{6.724 \text{ g sample}} \times 100 = 78.33\%$	1 point is earned for correct calculation of the mass percent based on the answer to part (g).

If the oxidation of the Fe(*s*) in the original sample was incomplete so that some of the 7.531 g of product was FeO(*s*) instead of $Fe_2O_3(s)$, would the calculated mass percent of Fe(*s*) in the original sample be higher, lower, or the same as the actual mass percent of Fe(*s*)? Justify your answer.

The calculated mass percent of Fe would be lower than the actual mass percent of Fe. ample that contains any FeO (rather than Fe_2O_3) will have a r actual mass percent of Fe than a completely oxidized sample would have. Therefore, when the moles of Fe are calculated (assuming all the mass of the sample is Fe_2O_3) the lculated number of moles of Fe, and hence the calculated mass percent of Fe, will be lower.	1 point is earned for the correct answer and a valid explanation.

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Question 4

Sulfur atom = ○ Carbon atom = ● Oxygen atom = ○

Compound	Molecular Structure	Boiling Point at 1 atm (K)
CS_2		319
COS		223

The table above gives the molecular structures and boiling points for the compounds CS_2 and COS.

In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $CS_2(l)$ is higher than that of $COS(l)$.

_ has only London dispersion forces, while COS has London dispersion forces and dipole-dipole forces. The London dispersion forces in CS_2 are stronger than the combination of London dispersion forces and dipole-dipole forces in COS.	1 point is earned for correctly identifying all of the intermolecular forces in **both** molecules. 1 point is earned for a valid explanation.

A 10.0 g sample of $CS_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $CS_2(l)$ has vaporized. What is the pressure in the container once all of the $CS_2(l)$ has vaporized?

$10.0\text{ g } CS_2 \times \frac{1\text{ mol } CS_2}{76.13\text{ g } CS_2} = 0.131\text{ mol } CS_2$ $\therefore \frac{nRT}{V} = \frac{(0.131\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{K}^{-1})(325\text{ K})}{5.0\text{ L}}$ $= 0.70\text{ atm}$	1 point is earned for the correct number of moles of 1 point is earned for the correct calculation of pressure with appropriate units.

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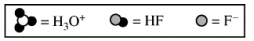
Question 5

$$HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$$

The ionization of $HF(aq)$ in water is represented by the equation above. In a 0.0350 M $HF(aq)$ solution, the percent ionization of HF is 13.0 percent.

Two particulate representations of the ionization of HF molecules in the 0.0350 M $HF(aq)$ solutio shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)



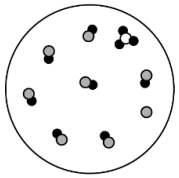


Figure 1

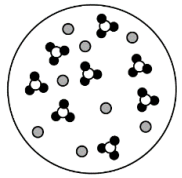


Figure 2

HF is a weak acid and is only partially ionized. This fact is consistent with Figure 1, which shows that one out of eight (~13%) HF molecules is ionized (to form one H_3O^+ and one F^-). Figure 2 cannot represent HF because it represents 100% ionization of the acid.	1 point is earned for a valid explanation.

Use the percent ionization data above to calculate the value of K_a for HF.

Assume $[H_3O^+] = [F^-]$ in $HF(aq)$. $\frac{[H_3O^+]}{0.0350\ M} = 0.130 \Rightarrow [H_3O^+] = 0.00455\ M$ $HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$ 0.0350 0 ~0 -0.00455 +0.00455 +0.00455 0.0304 0.00455 0.00455 $K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.00455)^2}{(0.0304)} = 6.81 \times 10^{-4}$	1 point is earned for the correct calculation of $[H_3O^+]$. 1 point is earned for a value of K_a consistent with the calculated value of $[H_3O^+]$.

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Question 5 (continued)

If 50.0 mL of distilled water is added to 50.0 mL of 0.035 *M* HF(*aq*), will the percent ionization HF(*aq*) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

The percent ionization of HF in the solution would increase. Doubling the volume of the solution decreases the initial concentration of each species by one-half; therefore, $\frac{(\frac{1}{2}[H_3O^+]_i)(\frac{1}{2}[F^-]_i)}{\frac{1}{2}[HF]_i} = \frac{1}{2}K_a \Rightarrow Q < K_a$. Consequently the equilibrium position will shift toward the products and increase the percent ionization. New volume = twice original volume, thus new $[HF]_i = \frac{0.035}{2} = 0.0175\ M$ $= \frac{[H_3O^+][F^-]}{[HF]} = 6.81 \times 10^{-4}$ (value from part (b)) Let $[H_3O^+] = [F^-] = x$ Then $6.81 \times 10^{-4} = \frac{(x)(x)}{(0.0175 - x)} \approx \frac{x^2}{(0.0175)} \Rightarrow x \approx 0.00345\ M$ Percent ionization $= \frac{0.00345\ M}{0.0175\ M} \times 100 = 20.\%$ $20\% > 13.0\%$; therefore, the percent ionization increases.	1 point is earned for correct answer valid explanation or calculation.

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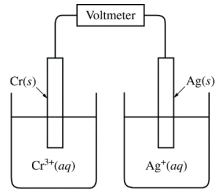
Question 6



A student sets up a galvanic cell at 298 K that has an electrode of Ag(*s*) immersed in a 1.0 *M* solution of $Ag^+(aq)$ and an electrode of Cr(*s*) immersed in a 1.0 *M* solution of $Cr^{3+}(aq)$, as shown in the diagram above.

The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

alt bridge is missing. The salt bridge allows for the migration of ions to maintain charge balance in each half-cell.	1 point is earned for the correct answer and a valid explanation.

Half-Reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	?

The student adds the missing component to the cell and measures E°_{cell} to be +1.54 V. As the cell operates, Ag^+ ions are reduced. Use this information and the information in the table above to do the following.

(i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$.

$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$ $+1.54\ V = +0.80\ V - x$ $= +0.80\ V - (+1.54\ V) = -0.74\ V$	1 point is earned for a correct calculation of E°_{red}.

(ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

$3\,Ag^+(aq) + Cr(s) \rightarrow 3\,Ag(s) + Cr^{3+}(aq)$	1 point is earned for the correctly balanced equation.

2018 SCORING GUIDELINES

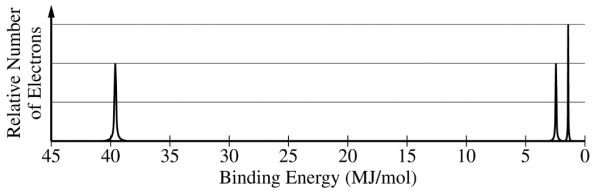
Question 6 (continued)

(iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol_{rxn}.

$\Delta G^\circ = -nFE^\circ = -\left(\frac{3 \text{ mol } e^-}{1 \text{ mol}_{rxn}}\right)\left(96{,}485\frac{\text{C}}{\text{mol } e^-}\right)\left(1.54\ \frac{\text{J}}{\text{C}}\right)$ $= -4.46 \times 10^5 \text{ J/mol}_{rxn}$	1 point is earned for the correct calculation of the value of Δ

2018 SCORING GUIDELINES

Question 7



The complete photoelectron spectrum of an element is represented above.

Identify the element.

The element is nitrogen, N.	1 point is earned for correctly identifying the element.

A radioactive isotope of the element decays with a half-life of 10. minutes.

Calculate the value of the rate constant, k, for the radioactive decay. Include units with your answer.

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10. \text{ min}} = 0.069 \text{ min}^{-1}$	1 point is earned for the correct numerical answer. 1 point is earned for the correct unit.

If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

$64 \rightarrow 32 \rightarrow 16 \rightarrow 8 \rightarrow 4 \rightarrow 2 \rightarrow 1$ 6 half-lives are required. $6 \times 10. \text{ min} = 60. \text{ min}$ **OR** $\ln[A]_t - \ln[A]_0 = -kt$ $t = \frac{\ln(1) - \ln(64)}{-0.069 \text{ min}^{-1}} = 60. \text{ min}$	1 point is earned for the correct answer and a valid method.

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)

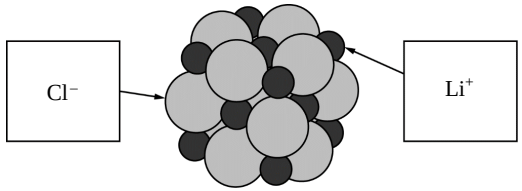
(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

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.

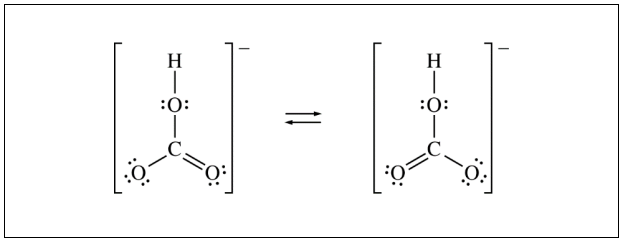
2016 SCORING GUIDELINES

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.

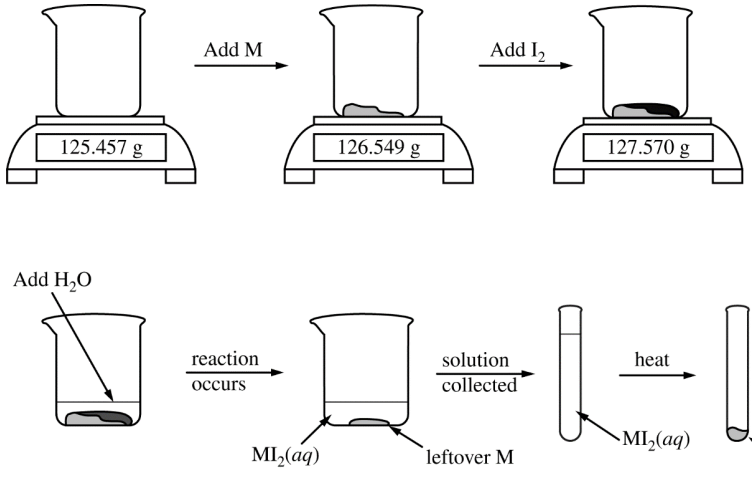
$C_2H_3O_2^- + H_3O^+ \rightarrow HC_2H_3O_2 + H_2O$ OR $C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$	1 point is earned for a correct equation.

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.

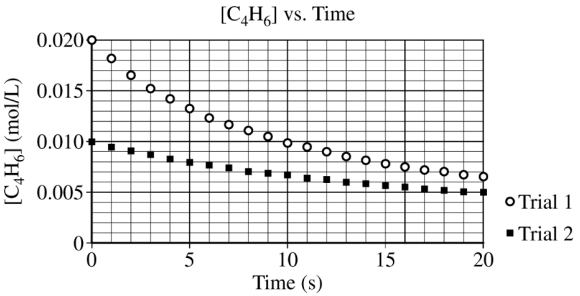
1 2 3 4 5 6 7 8 9 10 11 12 13 14

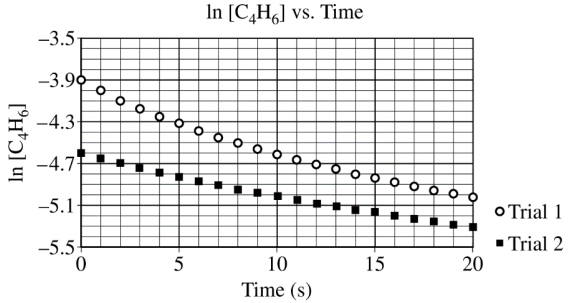
SCORING GUIDELINES

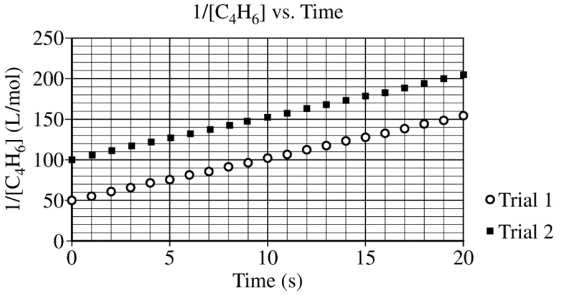
Question

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

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). $PV = nRT$ $P = \frac{nRT}{V} = \frac{(0.020 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(625 \text{ K})}{1.0 \text{ L}} = 1.0 \text{ atm}$	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). 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.

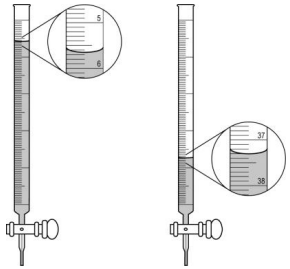
The number of moles of $Ba^{2+}(aq)$ increases because the percent dissociation of $Ba(EDTA)^{2-}(aq)$ increases as the solution is diluted. OR A mathematical justification such as the following: The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original 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

Question

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.