

Question 2: Long Answer

10 points

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

$$2.883 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 0.1600 \text{ mol H}_2\text{O}$$

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

$$0.1600 \text{ mol H}_2\text{O} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.3200 \text{ mol H}$$

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

Examples of acceptable responses may include the following:

- $x : y : z = (\text{moles of C}) : (\text{moles of H}) : (\text{moles of O})$
 $x : y : z = 0.2400 : 0.3200 : 0.2400 = 3 : 4 : 3$
Therefore, the empirical formula of ascorbic acid is C₃H₄O₃.

- $0.2400 \text{ mol CO}_2 \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.2400 \text{ mol C}$

$$\frac{0.3200 \text{ mol H}}{0.2400 \text{ mol C}} = \frac{4 \text{ H}}{3 \text{ C}}$$

Given that the ratio of C:O is 1:1, the empirical formula of ascorbic acid is C₃H₄O₃.

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

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

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

(ii) For the correct $\text{p}K_a$: **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:

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

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

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

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**

$$\text{rate} = k[\text{HAsc}][\text{I}_3^-]$$

Using trial 1 data:

$$k = \frac{\text{rate}}{[\text{HAsc}][\text{I}_3^-]} = \frac{2.457 \times 10^{-4} \text{ M/s}}{(0.450 \text{ M})(1.200 \text{ M})} = 4.55 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

For the correct units: **Point 09**

$$\text{M}^{-1} \text{ s}^{-1}$$

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

Ion-dipole attractions are present between I₃[−] ions and water but not between I₂ molecules and water.

Question 3: Long Answer

10 points

(a) For the correct balanced equation (state symbols not required): 1 point

Accept one of the following:

- $\text{CaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$
- $\text{CaCO}_3(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_2(g) + 3\text{H}_2\text{O}(l)$

(b) For a correct explanation: 1 point

Accept one of the following:

- Even though the concentration of HCl is greater in trial 5 than in trial 2, the reaction time is significantly longer. Both trial 2 and 5 occur under otherwise identical conditions. The trend for trial 1 and 4 indicates that the higher concentration of HCl results in a shorter time of reaction.*
- The time of reaction in trial 5, with small chunks of calcium carbonate, is longer than trial 6 with large chunks. Both trial 5 and 6 occur under otherwise identical conditions. The trend for trials 1, 2, and 3 shows that larger chunks of the solid result in longer time of reaction.*

(c) For a correct explanation of the effect of surface area on reaction time: 1 point

The time of reaction in trial 2 is shorter than that in trial 3 because the calcium carbonate in trial 2 has a larger surface area (meaning that more particles of calcium carbonate are exposed to the H^+ particles in the solution).

For a correct explanation of the effect of particle collisions on reaction rate: 1 point

The larger interface between the two reacting substances means there will be more collisions between the particles in a given amount of time, and thus, a higher frequency of successful collisions in which the particles react to form the products.

Total for part (c) 2 points

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

Accept one of the following:

- Disagree. If the reaction was zeroth order with respect to HCl, then changing the concentration of HCl would not affect the rate of reaction, and the time of reaction would be the same for trials in which the only difference was [HCl]. The student's data for trials 1 and 4 (likewise for 3 and 6) show that changing [HCl] significantly alters the time of reaction.*
- Disagree. The reaction appears to be first order, not zeroth order, with respect to [HCl]. Tripling [HCl] results in a reaction time that is 1/3 of that when [HCl] = 1.00 M, which means the reaction rate has also tripled, indicating a first-order process.*

(e) For the correct calculated moles of HCl reacted (may be implicit): 1 point

$$1.00 \text{ g CaCO}_3 \times \frac{1 \text{ mol}}{100.09 \text{ g}} = 0.00999 \text{ mol CaCO}_3$$

$$0.00999 \text{ mol CaCO}_3 \times \frac{2 \text{ mol HCl}}{1 \text{ mol CaCO}_3} = 0.0200 \text{ mol HCl reacted}$$

For the correct calculated [HCl] remaining, consistent with the number of moles reacted: 1 point

$$0.0500 \text{ L} \times \frac{1.00 \text{ mol HCl}}{1 \text{ L}} = 0.0500 \text{ mol HCl initially present}$$

$$0.0500 \text{ mol} - 0.0200 \text{ mol} = 0.0300 \text{ mol remaining}$$

$$\frac{0.0300 \text{ mol}}{0.0500 \text{ L}} = 0.600 \text{ M HCl remaining}$$

Total for part (e) 2 points

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

Exothermic. The solution temperature increases as the reaction proceeds.

(g) (i) For the correct calculated value (sign not required): 1 point

$$q_{\text{surr}} = mc\Delta T = (51.0 \text{ g})(4.0 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}})(21.90^\circ\text{C} - 21.20^\circ\text{C}) = 140 \text{ J}$$

(ii) For the correct calculated value, consistent with (g)(i), and the correct sign, consistent with (f): 1 point

$$q_{\text{sys}} = -q_{\text{surr}} = -140 \text{ J} = -0.14 \text{ kJ}$$

$$1.00 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \times \frac{1 \text{ mol rxn}}{1 \text{ mol CaCO}_3} = 0.00999 \text{ mol rxn}$$

$$\Delta H_{\text{rxn}}^\circ = \frac{-0.14 \text{ kJ}}{0.00999 \text{ mol rxn}} = -14 \text{ kJ/mol rxn}$$

Total for part (g) 2 points

Total for question 3 10 points

Question 5: Short Answer 4 points

(a) For the correct calculated value: 1 point

Accept one of the following:

- $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.67 \text{ hr}} = 0.415 \text{ hr}^{-1}$
- $k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.160) - \ln(0.0800)}{1.67 \text{ hr}} = 0.415 \text{ hr}^{-1}$
- $k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.160) - \ln(0.0400)}{3.33 \text{ hr}} = 0.416 \text{ hr}^{-1}$
- $k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.160) - \ln(0.0200)}{5.00 \text{ hr}} = 0.416 \text{ hr}^{-1}$

For the correct units, consistent with the calculated value: 1 point

 hr^{-1}

Total for part (a) 2 points

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

Step 1 is the rate-determining step. The rate law of elementary step 1 is $\text{rate} = k[\text{N}_2\text{O}_5]$, which is consistent with the first order kinetics of the overall rate law.

(c) For the correct answer: 1 point

Remain the same. The rate constant, k , is independent of concentration and will remain the same at constant temperature.

Total for question 5 4 points

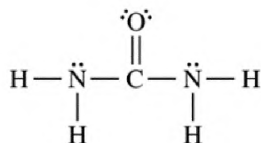
2019

AP[®] Chemistry

Scoring Guidelines

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Question 1

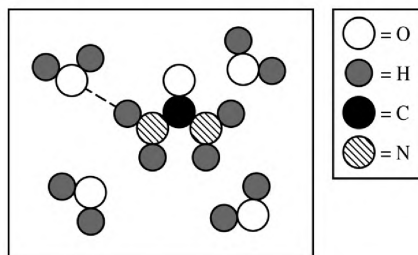


The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

- (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.

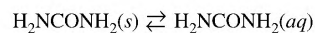
sp^2	1 point is earned for the correct answer.
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- (b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.



A dashed line should connect a hydrogen atom in water to a nitrogen or oxygen atom in urea or an oxygen atom in water to a hydrogen atom in urea. One possible correct response is shown above.

1 point is earned for a correct answer.



The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

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Question 1 (continued)

- (c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.

$$5.39 \text{ g H}_2\text{NCONH}_2 \times \frac{1 \text{ mol}}{60.06 \text{ g}} = 0.0897 \text{ mol}$$

$$\frac{0.0897 \text{ mol}}{0.00500 \text{ L}} = 17.9 \text{ M}$$

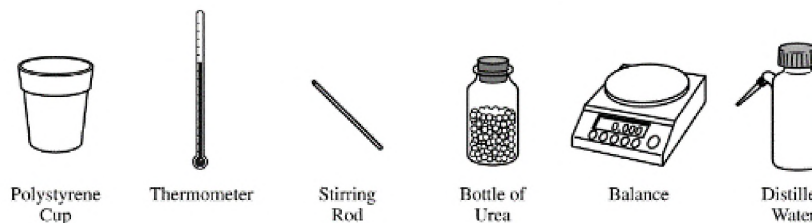
1 point is earned for the correct number of moles of urea (may be implicit).

1 point is earned for the correct molarity.

- (d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

The increased solubility at the higher temperature implies that the dissolution of urea is endothermic. If a saturated solution of urea is heated, then the equilibrium system is stressed. The stress is counteracted by the endothermic dissolution of more urea.

1 point is earned for the correct answer with an appropriate justification.



- (e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

mass of urea, mass of water, initial temperature of water, final temperature of solution

1 point is earned for the masses.

1 point is earned for the temperatures.

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Question 1 (continued)

	S° (J/(mol·K))
$\text{H}_2\text{NCONH}_2(s)$	104.6
$\text{H}_2\text{NCONH}_2(aq)$	?

- (f) The entropy change for the dissolution of urea, $\Delta S^\circ_{\text{soln}}$, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, S° , of aqueous urea.

$\Delta S^\circ_{\text{soln}} = S^\circ(\text{H}_2\text{NCONH}_2(aq)) - S^\circ(\text{H}_2\text{NCONH}_2(s))$ $70.1 \text{ J/(mol·K)} = S^\circ(\text{H}_2\text{NCONH}_2(aq)) - 104.6 \text{ J/(mol·K)}$ $S^\circ(\text{H}_2\text{NCONH}_2(aq)) = 174.7 \text{ J/(mol·K)}$	1 point is earned for the correct answer.
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- (g) Using particle-level reasoning, explain why $\Delta S^\circ_{\text{soln}}$ is positive for the dissolution of urea in water.

Urea molecules in solution have a greater number of possible arrangements than in solid urea. This increased number of arrangements corresponds to a positive $\Delta S^\circ_{\text{soln}}$.	1 point is earned for a correct explanation.
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- (h) The student claims that ΔS° for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

Thermodynamic favorability for a process at standard conditions is determined by the sign of ΔG° , with $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Since ΔS° is positive, the $T\Delta S^\circ$ term makes the value of ΔG° smaller and thus makes the dissolution more thermodynamically favorable.	1 point is earned for the correct answer.
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Question 2

Answer the following questions relating to the chemistry of the halogens.

- (a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

I_2 has the longest bond length because the radius of the I atom is greater than the radii of the other halogen atoms. Thus, the distance between the nuclei of atoms in I_2 is greater than it is in smaller halogens.	1 point is earned for circling I_2 and providing a valid explanation.
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A chemistry teacher wants to prepare Br_2 . The teacher has access to the following three reagents: $\text{NaBr}(aq)$, $\text{Cl}_2(g)$, and $\text{I}_2(s)$.

Half-Reaction	E° at 25°C (V)
$\text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^-$	1.07
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	1.36
$\text{I}_2 + 2 e^- \rightarrow 2 \text{I}^-$	0.53

- (b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of E° for the reaction.

$2 \text{Br}^- + \text{Cl}_2 \rightarrow \text{Br}_2 + 2 \text{Cl}^-$ $E^\circ = E^\circ(\text{reduced species}) - E^\circ(\text{oxidized species})$ $= 1.36 \text{ V} - 1.07 \text{ V} = +0.29 \text{ V}$ Because E° for the reaction has a positive value, the reaction is thermodynamically favorable.	1 point is earned for the correct balanced equation. 1 point is earned for the correct calculation of E°.
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Br_2 and Cl_2 can react to form the compound BrCl .

- (c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of each substance.

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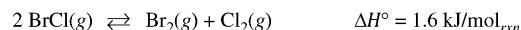
Question 2 (continued)

The only intermolecular attractions in $\text{Br}_2(l)$ are London forces, while those in $\text{BrCl}(l)$ include both London forces and dipole-dipole forces. However, due to the greater polarizability of the electron cloud of Br_2 compared to that of BrCl , the London forces in $\text{Br}_2(l)$ are stronger than the combined intermolecular forces in $\text{BrCl}(l)$. Thus, the boiling point of $\text{Br}_2(l)$ is greater than that of $\text{BrCl}(l)$.

1 point is earned for identifying the intermolecular forces in each substance.

1 point is earned for a valid explanation.

The compound BrCl can decompose into Br_2 and Cl_2 , as represented by the balanced chemical equation below.



A 0.100 mole sample of pure $\text{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

$$P = \frac{nRT}{V} = \frac{(0.100 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{2.00 \text{ L}} = 1.22 \text{ atm}$$

1 point is earned for a correct pressure with consistent units.

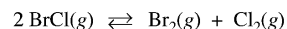
(e) Write the expression for the equilibrium constant, K_{eq} , for the decomposition of BrCl .

$$K_{eq} = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} \quad \text{or} \quad K_{eq} = \frac{P_{\text{Br}_2} P_{\text{Cl}_2}}{(P_{\text{BrCl}})^2}$$

1 point is earned for a correct equilibrium expression.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.



I	1.22	0	0
C	-2x	+x	+x
E	0.71	0.26	0.26

$$P_{\text{BrCl decomposed}} = (0.42)(1.22 \text{ atm}) = 0.51 \text{ atm}$$

$$2x = 0.51 \text{ atm} \Rightarrow x = 0.26 \text{ atm}$$

$$K_{eq} = \frac{(0.26)(0.26)}{(0.71)^2} = 0.13$$

Note: The solution is in terms of pressures. Solutions in terms of molar concentrations also earn full credit.

1 point is earned for correct stoichiometric values at equilibrium.

1 point is earned for a consistent value of K_{eq} .

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Question 2 (continued)

Calculate the bond energy of the Br-Cl bond, in kJ/mol , using ΔH° for the reaction (1.6 kJ/mol information in the following table.

Bond	Bond Energy (kJ/mol)
$\text{Br}-\text{Br}$	193
$\text{Cl}-\text{Cl}$	243
$\text{Br}-\text{Cl}$	?

$$\Delta H^\circ = \sum (\text{bond energies})_{\text{broken}} - \sum (\text{bond energies})_{\text{formed}}$$

$$\text{J/mol} = 2(\text{Br-Cl bond energy}) - (193 \text{ kJ/mol} + 243 \text{ kJ/mol})$$

$$36 + 1.6 \text{ kJ/mol} = 2(\text{Br-Cl bond energy})$$

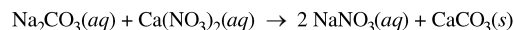
$$\text{Cl bond energy} = 219 \text{ kJ/mol}$$

1 point is earned for a correct calculation of the Br-Cl bond energy.

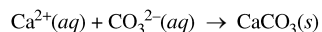
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Question 3

A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $\text{Ca}(\text{NO}_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

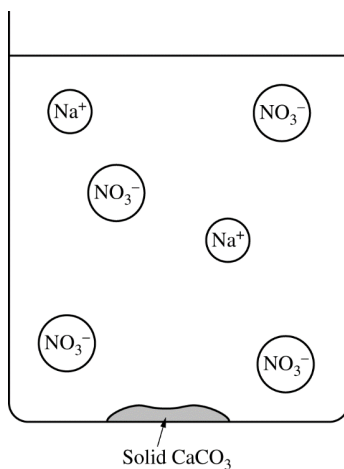


Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $\text{Ca}(\text{NO}_3)_2$ are mixed.



1 point is earned for the correct equation.

The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The drawing shows one Ca^{2+} ion.

1 point is earned for drawing a Ca^{2+} ion.

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Question 3 (continued)

The student filters and dries the precipitate of CaCO_3 (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $\text{Ca}(\text{NO}_3)_2$ added	100.0 mL
Mass of CaCO_3 precipitate collected	0.93 g

Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

$$0.93 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g}} = 0.0093 \text{ mol CaCO}_3$$

$$0.0093 \text{ mol CaCO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CaCO}_3} = 0.0093 \text{ mol Na}_2\text{CO}_3$$

1 point is earned for the correct answer.

The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

Disagree. The presence of water in the solid will cause the measured mass of the precipitate to be greater than the actual mass of CaCO_3 . As a result, the calculated number of moles of CaCO_3 and moles of Na_2CO_3 will be greater than the actual moles present. Therefore the calculated concentration of $\text{Na}_2\text{CO}_3(aq)$ will be too high.

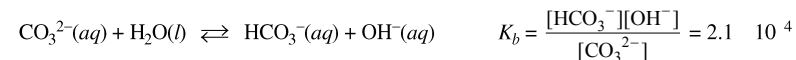
1 point is earned for the correct answer with valid justification.

After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The liquid conducts electricity because ions ($\text{Na}^+(aq)$, $\text{NO}_3^-(aq)$, and $\text{Na}^+(aq)$) are present in the solution.

1 point is earned for the correct answer with valid justification.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When it is dissolved in water, $\text{CO}_3^{2-}(aq)$ hydrolyzes to form $\text{HCO}_3^-(aq)$, as shown by the following equation.



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Question 3 (continued)

The student decides to first determine $[\text{OH}^-]$ in the solution, then use that result to calculate the initial concentration of $\text{CO}_3^{2-}(\text{aq})$.

- (i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[\text{OH}^-]$ in the solution.

Determine the pH of the solution using a pH meter.	1 point is earned for identifying a valid method.
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- (ii) Explain how the student could use the measured value in part (f)(i) to calculate the initial concentration of $\text{CO}_3^{2-}(\text{aq})$. (Do not do any numerical calculations.)

First determine $[\text{OH}^-]$ using $\text{pOH} = 14 - \text{pH}$, then $[\text{OH}^-] = 10^{-\text{pOH}}$.

use the K_b expression and an ICE table (see example below) to determine $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$ at equilibrium. The initial concentration of CO_3^{2-} , c_i , is equal to the sum of the equilibrium concentrations of CO_3^{2-} and HCO_3^- .

	$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$	
	c_i	---	0	0
	$-x$	---	$+x$	$+x$
	$c_i - x$	---	x	x

$$K_b = \frac{(x)(x)}{c_i - x} \Rightarrow c_i = \frac{(x)(x)}{K_b} + x$$

1 point is earned for a valid method of determining $[\text{OH}^-]$ from the measured value.

1 point is earned for a valid method of determining the initial concentration of CO_3^{2-} .

In the original Na_2CO_3 solution at equilibrium, is the concentration of $\text{HCO}_3^-(\text{aq})$ greater than, less than, or equal to the concentration of $\text{CO}_3^{2-}(\text{aq})$? Justify your answer.

Less than. The small value of K_b , 2.1×10^{-4} , indicates the reactants are favored.	1 point is earned for the correct answer with a valid justification.
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The student needs to make a $\text{CO}_3^{2-}/\text{HCO}_3^-$ buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

The Na_2CO_3 solution is not suitable. The $\text{p}K_a$ of HCO_3^- is 10.32. Buffers are effective when the required pH is approximately equal to the $\text{p}K_a$ of the weak acid. An acid with a $\text{p}K_a$ of 10.32 is not appropriate to prepare a buffer with a pH of 6.	1 point is earned for the correct answer with a valid explanation.
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Question 4

The student is doing experiments with $\text{CO}_2(\text{g})$. Originally, a sample of the gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the $\text{CO}_2(\text{g})$ in the container to 425 K.

Describe the effect of raising the temperature on the motion of the $\text{CO}_2(\text{g})$ molecules.

The average speed of the molecules increases as temperature increases.	1 point is earned for the correct answer.
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Calculate the pressure of the $\text{CO}_2(\text{g})$ in the container at 425 K.

Both the volume and the number of molecules are constant, therefore

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{0.70 \text{ atm}}{299 \text{ K}} = \frac{P_2}{425 \text{ K}} \Rightarrow P_2 = 0.99 \text{ atm}$$

1 point is earned for the correct answer.

In terms of kinetic molecular theory, briefly explain why the pressure of the $\text{CO}_2(\text{g})$ in the container changes as it is heated to 425 K.

Faster-moving gas particles collide more frequently with the walls of the container, thus increasing the pressure.

Faster-moving gas particles collide more forcefully with the walls of the container, thus increasing the pressure.

1 point is earned for a correct explanation.

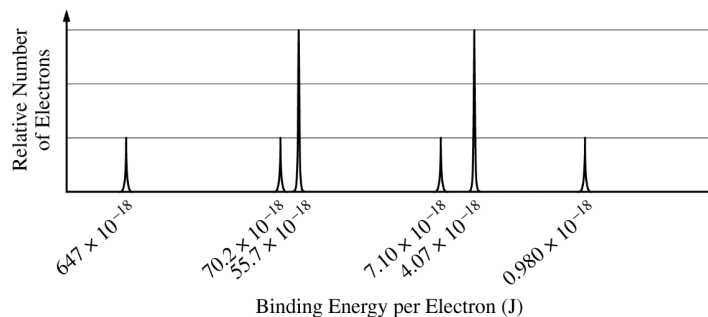
The student measures the actual pressure of the $\text{CO}_2(\text{g})$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

The attractive forces between CO_2 molecules result in a pressure that is lower than that predicted by the ideal gas law.	1 point is earned for a correct explanation.
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Question 5

The complete photoelectron spectrum of an element in its ground state is represented below.



Based on the spectrum,

(i) write the ground-state electron configuration of the element, and

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[\text{Ar}] 4s^2$

1 point is earned for the correct answer.

(ii) identify the element.

Ca

1 point is earned for the correct answer.

Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of the element.

Energy (E) required = $0.980 \times 10^{-18} \text{ J}$

$$E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ ms}^{-1})}{0.980 \times 10^{-18} \text{ J}}$$

$$\lambda = 2.03 \times 10^{-7} \text{ m}$$

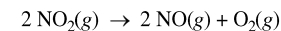
1 point is earned for the correct identification of the energy required to remove an electron from the valence shell (may be implicit).

1 point is earned for calculating the correct wavelength.

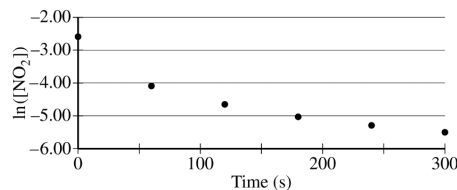
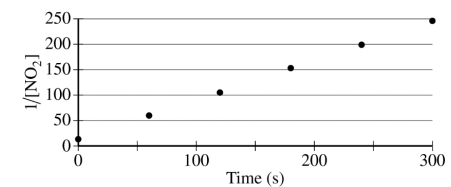
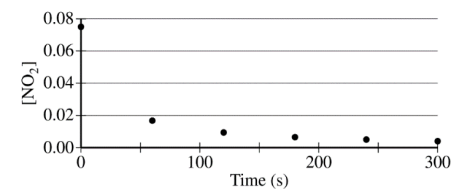
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Question 6

Nitrogen dioxide, $\text{NO}_2(\text{g})$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $\text{NO}_2(\text{g})$ decomposes according to the equation below.



The concentration of a sample of $\text{NO}_2(\text{g})$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.



Explain how the graphs indicate that the reaction is second order.

The linear graph of $\frac{1}{[\text{NO}_2]}$ vs. time indicates a second-order reaction.

1 point is earned for the correct answer.

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Question 6 (continued)

Write the rate law for the decomposition of $\text{NO}_2(\text{g})$.

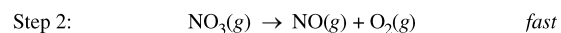
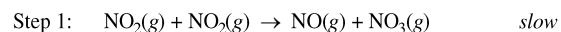
$$\text{rate} = k[\text{NO}_2]^2$$

1 point is earned for the correct answer.

Consider two possible mechanisms for the decomposition reaction.

- (i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

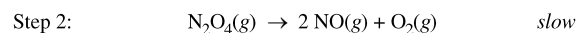


Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is $\text{rate} = k[\text{NO}_2][\text{NO}_2] = k[\text{NO}_2]^2$, which is consistent with the second-order rate law in part (b).

1 point is earned for the correct answer with justification.

- (ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II

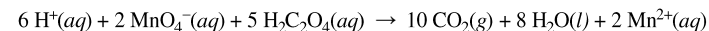


Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is $\text{rate} = k[\text{N}_2\text{O}_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$ in step 1, $[\text{N}_2\text{O}_4] = K_{eq}[\text{NO}_2]^2$. Then, substituting $K_{eq}[\text{NO}_2]^2$ for $[\text{N}_2\text{O}_4]$ in the rate law of step 2 gives $\text{rate} = (k K_{eq})[\text{NO}_2]^2$, which is consistent with the rate law in part (b).

1 point is earned for the correct answer with justification.

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Question 7



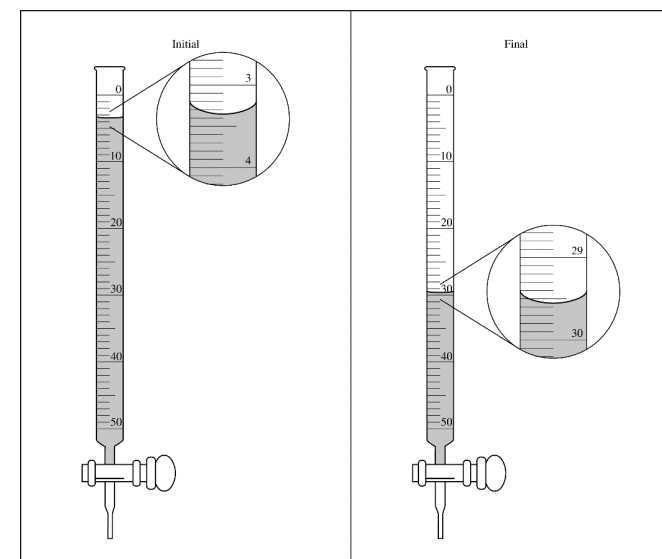
A student dissolved a 0.139 g sample of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, in water in an Erlenmeyer flask. Then the student titrated the $\text{H}_2\text{C}_2\text{O}_4$ solution in the flask with a solution of KMnO_4 , which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown above.

Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

MnO_4^- is reduced to Mn^{2+} as the oxidation number of Mn changes from +7 to +2, indicating a gain of 5 electrons.

1 point is earned for the correct answer with justification.

The student used a 50.0 mL buret to add the $\text{KMnO}_4(\text{aq})$ to the $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$ until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $\text{KMnO}_4(\text{aq})$ that was added during the titration.



$$29.55 \text{ mL} - 3.55 \text{ mL} = 26.20 \text{ mL}$$

1 point is earned for the correct answer.

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Question 7 (continued)

Given that the concentration of $\text{KMnO}_4(aq)$ was 0.0235 M , calculate the number of moles of MnO^- ions that completely reacted with the $\text{H}_2\text{C}_2\text{O}_4$.

$$(0.02620\text{ L})(0.0235\text{ mol/L}) = 0.000616\text{ mol}$$

1 point is earned for the correct answer.

The student proposes to perform another titration using a 0.139 g sample of $\text{H}_2\text{C}_2\text{O}_4$, but this time using 0.00143 M $\text{KMnO}_4(aq)$ in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

No. The 0.00143 M titrant solution is so diluted that volume of titrant needed to reach the end point would be much greater than the 50 mL capacity of the buret.

1 point is earned for the correct answer with appropriate justification.

2017

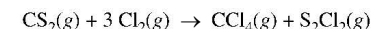
AP CollegeBoard

AP Chemistry

Scoring Guidelines

2017 SCORING GUIDELINES

Question 1



Carbon tetrachloride, $\text{CCl}_4(g)$, 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, $\text{Cl}_2(g)$, is initially present in the container at a pressure of 0.40 atm .

(i) How many moles of $\text{Cl}_2(g)$ 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, $\text{CS}_2(g)$, are needed to react completely with the $\text{Cl}_2(g)$?

$$0.31\text{ mol Cl}_2 \times \frac{1\text{ mol CS}_2}{3\text{ mol Cl}_2} \times \frac{76.13\text{ g CS}_2}{1\text{ mol CS}_2} = 7.9\text{ g CS}_2$$

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.

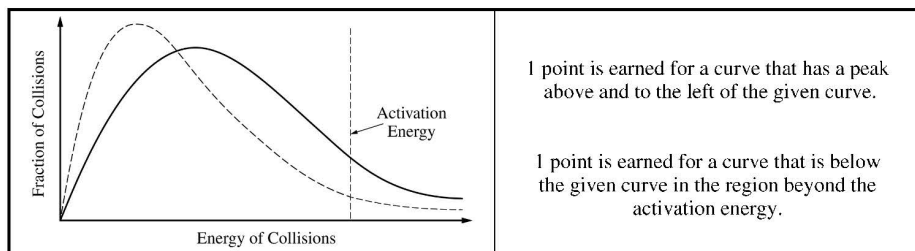
(i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C .

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.

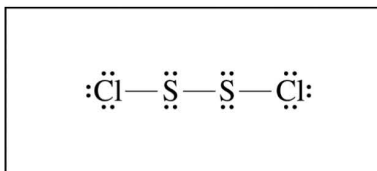
(ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C .

Question 1 (continued)



(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.

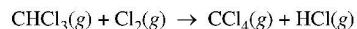
1 point is earned for a correctly drawn diagram.

(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) $\text{CCl}_4(g)$ can also be produced by reacting $\text{CHCl}_3(g)$ with $\text{Cl}_2(g)$ at 400°C , as represented by the equation below.



At the completion of the reaction a chemist successfully separates the $\text{CCl}_4(g)$ from the $\text{HCl}(g)$ by cooling the mixture to 70°C , at which temperature the $\text{CCl}_4(g)$ condenses while the $\text{HCl}(g)$ remains in the gaseous state.

Question 1 (continued)

(i) Identify all types of intermolecular forces present in $\text{HCl}(l)$.

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 $\text{CCl}_4(l)$ and $\text{HCl}(l)$? 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.

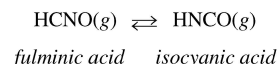
In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of -1 . In the diagram on the right, the C atom has a formal charge of -1 and the O atom has a formal charge of zero.

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 assignment of formal charges in the two diagrams.

1 point is earned for a correct explanation.

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



Fulminic Acid		Isocyanic Acid	
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$		$\text{H}-\ddot{\text{C}}=\text{N}=\ddot{\text{O}}:$	

- (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

$$\begin{aligned}\Delta H^\circ &= \Sigma(\text{enthalpies of bonds broken}) - \Sigma(\text{enthalpies of bonds formed}) \\ &= 1505 \text{ kJ/mol} - 1751 \text{ kJ/mol} \\ &= -246 \text{ kJ/mol}_{\text{rxn}}\end{aligned}$$

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 ΔS° 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.

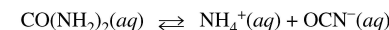
Isocyanic acid (HNCO) will be present in higher concentration.
 ΔG° is essentially equal to ΔH° because ΔS° is essentially zero, so $\Delta G^\circ \approx -246 \text{ kJ/mol}_{\text{rxn}}$, indicating the forward reaction is thermodynamically favorable.

Since ΔG° is negative, $K > 1$ ($\Delta G^\circ = -RT \ln K$), 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 ΔG° is a sufficient justification.)

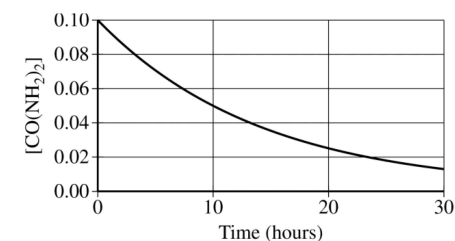
1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K .

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



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)	$[\text{CO}(\text{NH}_2)_2]$
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.

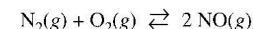
(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

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



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.

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$$

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 .

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

$$2x = 0.122 \text{ atm} \Rightarrow x = 0.0610 \text{ atm}$$

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

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.

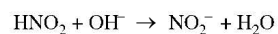
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(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.



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,

$[\text{HNO}_2] = [\text{NO}_2^-]$, therefore the buffer has a pH equal to $\text{p}K_a$.

OR

$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$, thus $\text{pH} = \text{p}K_a$ when $[\text{HNO}_2] = [\text{NO}_2^-]$

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).

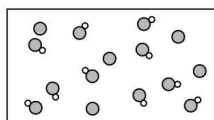
- (d) A second student makes a buffer by dissolving 0.100 mol of NaNO_2 (s) in 100. mL of 1.00 M HNO_2 (aq). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.

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.

● HNO_2 molecule ● NO_2^- ion



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Question 3 (continued)

The pH of the solution is less than 3.40.

If $[\text{HNO}_2] = [\text{NO}_2^-]$, $\text{pH} = \text{p}K_a$, and the pH of the solution would be 3.40.

Since $[\text{HNO}_2] > [\text{NO}_2^-]$, as represented in the diagram, the solution has a pH less than 3.40.

OR

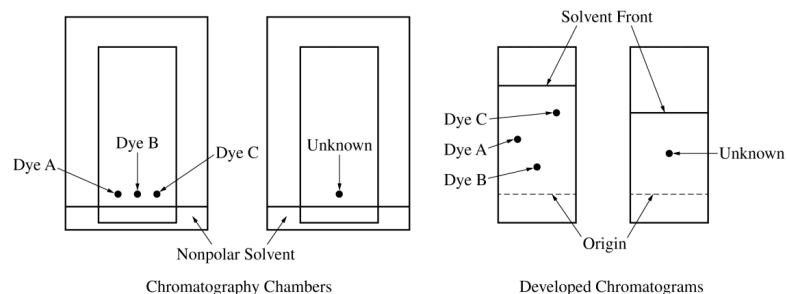
$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \Rightarrow \text{pH} = 3.40 + \log \frac{5}{10} \Rightarrow \text{pH} = 3.10$$

1 point is earned for the correct choice.

1 point is earned for a valid justification.

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Question 4



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.

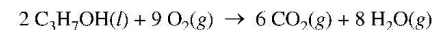
Dye C is the least polar because it moved the farthest.	1 point is earned for the correct choice and reference to the chromatogram.
Nonpolar dyes are more strongly attracted to the nonpolar solvent. AND/OR Nonpolar dyes are least strongly retained by the polar paper.	1 point is earned for a correct description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

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

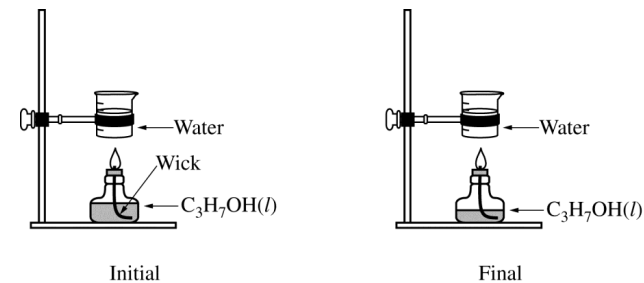
Dye A is present in the unknown sample.	1 point is earned for the correct choice.
The unknown sample moves to a position that is midway between the origin and the solvent front, and so does dye A. OR Dye A has a retention factor (R_f) that is close to 0.50 on the chromatogram with the three dyes, and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

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Question 5



A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $\text{C}_3\text{H}_7\text{OH}(l)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $\text{C}_3\text{H}_7\text{OH}(l)$ 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 $\text{C}_3\text{H}_7\text{OH}(l)$ combusted is determined by weighing the alcohol burner before and after combustion.



Data from the experiment are given in the table below.

Mass of $\text{C}_3\text{H}_7\text{OH}(l)$ 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.)

$q = mc\Delta T$ $= (125.00 \text{ g})(4.18 \text{ J/(g}\cdot\text{°C)})(51.1^\circ\text{C} - 22.0^\circ\text{C})$ $= 15,200 \text{ J} = 15.2 \text{ kJ}$	1 point is earned for the correct calculation.
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2017 SCORING GUIDELINES

Question 5 (continued)

- (b) Based on the experimental data, if one mole of $\text{C}_3\text{H}_7\text{OH}(l)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.

$1 \text{ mol C}_3\text{H}_7\text{OH} \times \frac{60.09 \text{ g C}_3\text{H}_7\text{OH}}{1 \text{ mol C}_3\text{H}_7\text{OH}} \times \frac{15.2 \text{ kJ}}{0.55 \text{ g C}_3\text{H}_7\text{OH}} = 1661 \text{ kJ}$ $= 1.7 \times 10^3 \text{ kJ}$	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.
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- (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 $\text{C}_3\text{H}_7\text{OH}(l)$ that is contaminated with water, which is miscible with $\text{C}_3\text{H}_7\text{OH}(l)$. 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 $\text{C}_3\text{H}_7\text{OH}(l)$ 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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2017 SCORING GUIDELINES

Question 6

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

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

$1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (x)(2x)^2 = 4x^3$ $x = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.65 \times 10^{-4} \text{ M} = [\text{Mg}^{2+}] = [\text{Mg}(\text{OH})_2]$ $0.100 \text{ L} \times \frac{1.65 \times 10^{-4} \text{ mol}}{1 \text{ L}} \times \frac{58.32 \text{ g Mg}(\text{OH})_2}{1 \text{ mol Mg}(\text{OH})_2} = 9.6 \times 10^{-4} \text{ g Mg}(\text{OH})_2$	1 point is earned for calculating the solubility of $\text{Mg}(\text{OH})_2$. 1 point is earned for calculating the correct mass based on the solubility of $\text{Mg}(\text{OH})_2$.
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- (b) The energy required to separate the ions in the $\text{Mg}(\text{OH})_2$ crystal lattice into individual $\text{Mg}^{2+}(g)$ and $\text{OH}^-(g)$ ions, as represented in the table below, is known as the lattice energy of $\text{Mg}(\text{OH})_2(s)$. As shown in the table, the lattice energy of $\text{Sr}(\text{OH})_2(s)$ is less than the lattice energy of $\text{Mg}(\text{OH})_2(s)$. Explain why in terms of periodic properties and Coulomb's law.

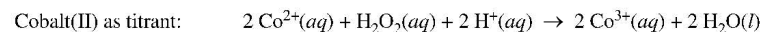
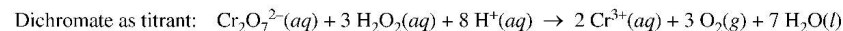
Reaction	Lattice Energy (kJ/mol)
$\text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(g) + 2 \text{ OH}^-(g)$	2900
$\text{Sr}(\text{OH})_2(s) \rightarrow \text{Sr}^{2+}(g) + 2 \text{ OH}^-(g)$	2300

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 $\text{Mg}(\text{OH})_2$ 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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2017 SCORING GUIDELINES

Question 7

A student wants to determine the concentration of H_2O_2 in a solution of $\text{H}_2\text{O}_2(aq)$. The student can use one of two titrants, either dichromate ion, $\text{Cr}_2\text{O}_7^{2-}(aq)$, or cobalt(II) ion, $\text{Co}^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.



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
$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$	1.84
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.77
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70

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

(i) E° for the reaction between $\text{Cr}_2\text{O}_7^{2-}(aq)$ and $\text{H}_2\text{O}_2(aq)$ at 298 K

$E^\circ = 1.33 - 0.70 = 0.63 \text{ V}$	1 point is earned for correctly combining E° values.
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(ii) E° for the reaction between $\text{Co}^{2+}(aq)$ and $\text{H}_2\text{O}_2(aq)$ at 298 K

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

$\Delta G^\circ = -nFE^\circ$ and n , F , and E° are all positive numbers, therefore $\Delta G^\circ < 0$, 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 ΔG° is required.

(ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction between the chosen titrant and $\text{H}_2\text{O}_2(aq)$.

$$\Delta G^\circ = -nFE^\circ = -6(96,485 \frac{\text{C}}{\text{mol}})(0.63 \frac{\text{J}}{\text{C}})(\frac{1 \text{ kJ}}{1000 \text{ J}}) = -360 \text{ kJ/mol}_{\text{rxn}}$$

1 point is earned for calculating the value of ΔG° .

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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 $\pm 0.1^\circ\text{C}$.

- (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 $4.18 \text{ J/(g}\cdot^\circ\text{C)}$. Include units with your answer.

$$q = mc\Delta T = (110.0 \text{ g})(4.18 \text{ J/(g}\cdot^\circ\text{C)})(35.6^\circ\text{C} - 15.0^\circ\text{C})$$

$$= 9,470 \text{ J} = 9.47 \text{ kJ}$$

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} .

$$10.0 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} = 0.236 \text{ mol LiCl}$$

$$\frac{-9.47 \text{ kJ}}{0.236 \text{ mol LiCl}} = -40.1 \text{ kJ/mol}_{rxn}$$

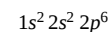
1 point is earned for the number of moles of LiCl.

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.



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.

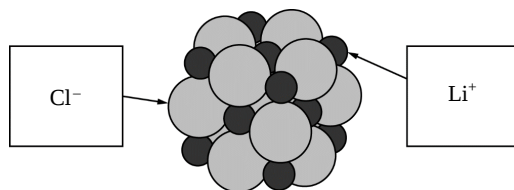
1 point is earned for a correct explanation based on occupied principal energy levels.

- (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. 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.

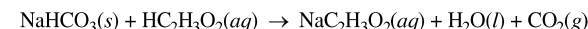
These are ion-dipole interactions.

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



A student designs an experiment to study the reaction between NaHCO_3 and $\text{HC}_2\text{H}_3\text{O}_2$. 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 $\text{HC}_2\text{H}_3\text{O}_2$. 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 $\text{HC}_2\text{H}_3\text{O}_2$ reacts with the weak base HCO_3^- with $\text{HC}_2\text{H}_3\text{O}_2$ donating a proton.

1 point is earned for identifying the reaction as acid-base.

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 the justification.

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

$$2.24 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.0 \text{ g}} = 0.0267 \text{ mol NaHCO}_3$$

1 point is earned for calculating the number of moles of each reactant.

$$60.0 \text{ mL} \times \frac{0.875 \text{ mol HC}_2\text{H}_3\text{O}_2}{1000 \text{ mL}} = 0.0525 \text{ mol HC}_2\text{H}_3\text{O}_2$$

The $\text{NaHCO}_3(s)$ and $\text{HC}_2\text{H}_3\text{O}_2(aq)$ react in a 1:1 ratio, so the limiting reactant is $\text{NaHCO}_3(s)$.

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 concentrations 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
- $\text{NaHCO}_3(s)$
- and
- $\text{HC}_2\text{H}_3\text{O}_2(aq)$
- ? 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)

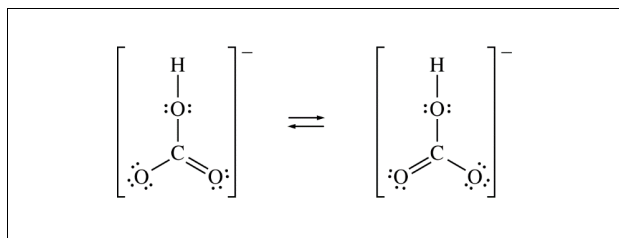
(ii) Justify your selection in part (d)(i) in terms of ΔG° .

$$\Delta = \Delta H^\circ - T\Delta S^\circ$$

Reactions are thermodynamically favorable when ΔG° is negative. Since the reaction is endothermic (the flask gets cooler, ΔH° is positive), the reaction is not driven by enthalpy, because enthalpy does not help make ΔG° negative. Because there are no gases in the reactants and one of the products is a gas, ΔS° must be positive, which helps make ΔG° 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.

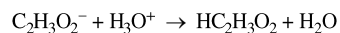


See diagram above.

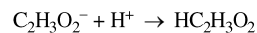
1 point is earned for a correct Lewis structure of HCO_3^- .

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 $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $\text{HNO}_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $\text{HNO}_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.



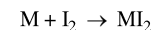
OR



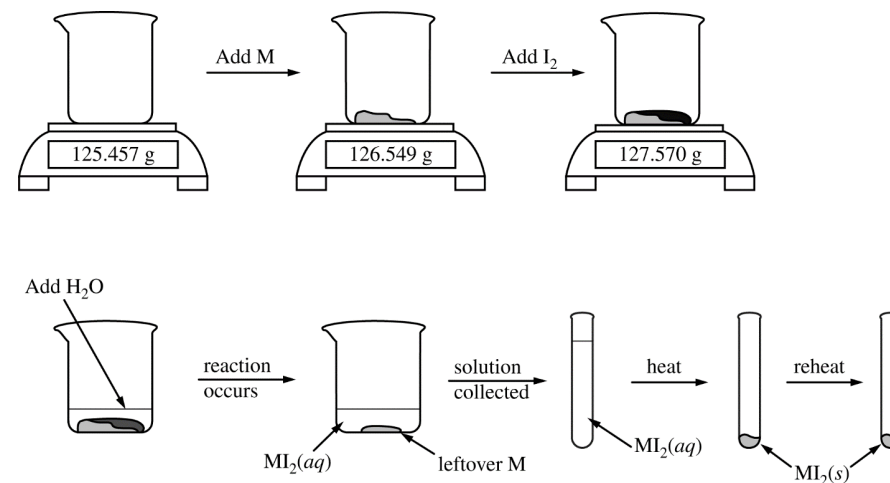
1 point is earned for a correct equation.

SCORING GUIDELINES

Question



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 $\text{MI}_2(aq)$ 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.
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- (b) Calculate the molar mass of the unknown metal M.

Number of moles of I_2 = number of moles of M $1.284 \text{ g } MI_2 - 1.021 \text{ g } I_2 = 0.263 \text{ g M}$ $\text{Molar mass of M} = \frac{0.263 \text{ g M}}{0.004023 \text{ mol M}} = 65.4 \text{ g/mol}$	1 point is earned for the number of grams of M. 1 point is earned for the molar mass.
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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.
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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)
$S_4O_6^{2-}(aq) + 2e^- \rightarrow 2S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	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.

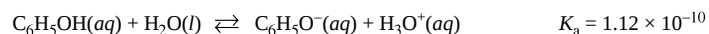
$H_2O_2(aq)$	$Na_2S_2O_3(aq)$	$Na_2S_4O_6(aq)$
[Na $_2S_2O_3(aq)$ should be circled.] The reaction between $S_2O_3^{2-}(aq)$ and $I_2(s)$ will be thermodynamically favorable because E° for the reaction is positive ($E^\circ = 0.54 - 0.08 = +0.46 \text{ V}$), from which it follows that ΔG° is negative because $\Delta G^\circ = -nFE^\circ$.	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).

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

Question



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 $\text{C}_6\text{H}_5\text{OH}(aq)$ solution?

$K_a = \frac{[\text{C}_6\text{H}_5\text{O}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{OH}]}$ $1.12 \times 10^{-10} = \frac{x^2}{(0.75 - x)} \quad \text{Assume that } x \ll 0.75.$ $x^2 = 8.4 \times 10^{-11}$ $x = \sqrt{8.4 \times 10^{-11}}$ $x = 9.2 \times 10^{-6} \text{ M}$ $\text{pH} = -\log[\text{H}^+] = -\log(9.2 \times 10^{-6}) = 5.04$	1 point is earned for a correct setup and calculation of $[\text{H}^+]$. 1 point is earned for the correct setup and calculation of pH based on a correct setup for the $[\text{H}^+]$ calculation.
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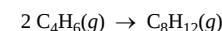
(b) For a certain reaction involving $\text{C}_6\text{H}_5\text{OH}(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $\text{C}_6\text{H}_5\text{O}^-(aq)$. In order to ensure that the $\text{C}_6\text{H}_5\text{OH}(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle each pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($\text{C}_6\text{H}_5\text{O}^-(aq)$). Justify your answer.

Numbers 10 through 14 should be circled. When $\text{pH} > \text{p}K_a$, the deprotonated form will predominate. $\text{p}K_a = -\log(1.12 \times 10^{-10}) = 9.95$, therefore at pH 10 and above, $[\text{C}_6\text{H}_5\text{O}^-] > [\text{C}_6\text{H}_5\text{OH}]$.	1 point is earned for circling 10–14. 1 point is earned for the justification.
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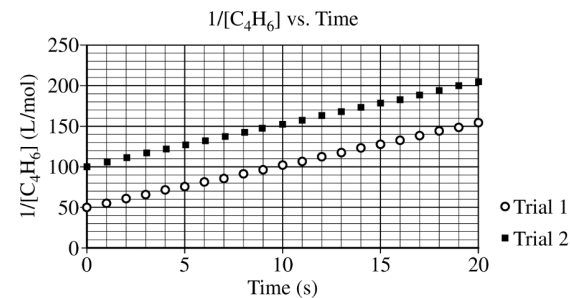
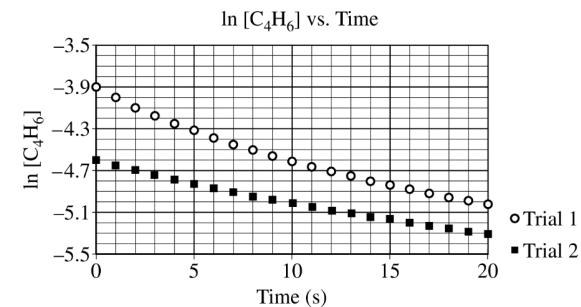
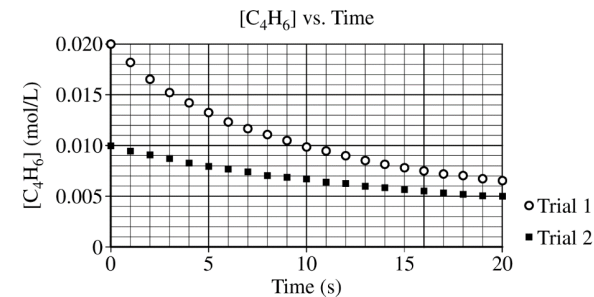
1 2 3 4 5 6 7 8 9 10 11 12 13 14

SCORING GUIDELINES

Question



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, $\frac{n}{V} = 0.020 \text{ mol/L}$ (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).	1 point is earned for a correct setup.
$PV = nRT$	
$P = \frac{nRT}{V} = \frac{(0.020 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(625 \text{ K})}{1.0 \text{ L}} = 1.0 \text{ atm}$	1 point is earned for 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): $\text{rate} = k[C_4H_6]^2$ $\Rightarrow k = \frac{\text{rate}}{([C_4H_6])^2} = \frac{0.0010 \text{ mol/(L} \cdot \text{s)}}{(0.020 \text{ mol/L})^2} = 2.5 \text{ L/(mol} \cdot \text{s)}$ 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 = $5.0 \text{ L/(mol} \cdot \text{s)} = 2k$, therefore $k = 2.5 \text{ L/(mol} \cdot \text{s)}$. <u>Note:</u> Students who choose the second method of determining k but omit the factor of 2, thereby getting an answer of $5.0 \text{ L/(mol} \cdot \text{s)}$, still earn the point.	1 point is earned for the correct value.
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SCORING GUIDELINES

Question



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.

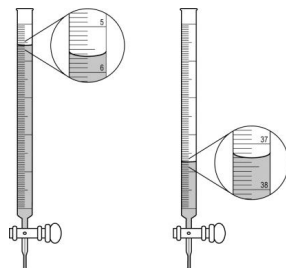
The number of moles of $Ba^{2+}(aq)$ increases because the percent dissociation of $Ba(EDTA)^{2-}(aq)$ increases as the solution is diluted. OR A mathematical justification such as the following: The dilution from 100.0 mL to 1.00 L reduces the concentrations of all species to one tenth of their original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



$$37.30 \text{ mL} - 5.65 \text{ mL} = 31.65 \text{ mL}$$

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:

$$(0.110 \text{ M})(0.03165 \text{ L}) \times \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} \times \frac{1}{0.0250 \text{ L}} = 0.139 \text{ M}$$

OR

$$\text{moles of } \text{H}^+ \text{ consumed} = M_a V_a$$

$$M_a V_a = M_b V_b$$

$$\text{Therefore, } M_a = \frac{M_b V_b}{V_a} = \frac{(0.110 \text{ M})(0.03165 \text{ L})}{0.0250 \text{ L}} = 0.139 \text{ M}$$

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.

AP[®] Chemistry

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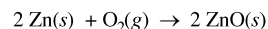
SCORING GUIDELINES

Question

Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	E at pH 11 and 298 K (V)
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.34
$\text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s}) + 2 \text{OH}^-(\text{aq})$	-1.31
$\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Na}(\text{s}) + 2 \text{OH}^-(\text{aq})$	-1.60
$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s}) + 2 \text{OH}^-(\text{aq})$	-2.78

Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.



(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

$E_{\text{cell}} = 0.34 \text{ V} - (-1.31 \text{ V}) = 1.65 \text{ V}$	1 point is earned for the correct cell potential.
---	---

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(The arrow should point to the left.)	1 point is earned for indicating the movement of OH^- ions from right to left in the cell.
---------------------------------------	---

A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

The mass increases.	1 point is earned for indicating an increase in cell mass.
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(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

Oxygen gas from the air reacts with $\text{Zn}(\text{s})$ in the cell, producing $\text{ZnO}(\text{s})$, which has more mass than the original $\text{Zn}(\text{s})$.	1 point is earned for the justification.
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SCORING GUIDELINES

Question 1 (continued)

The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

The cell potential will be lower.	1 point is earned for indicating a lower cell potential.
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(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

$\text{O}_2(\text{g})$, a reactant in the cell reaction, will be at a lower partial pressure at the higher elevation; thus the reaction has a greater value of Q (closer to K). Deviations in partial pressure that take the cell closer to equilibrium will decrease the magnitude of the cell potential.	1 point is earned for a justification that relates lower pressure (or concentration) of O_2 (or a qualitative approach using the Nernst equation).
--	---

Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

$\text{Na, } 1.0 \text{ g Na} \times \frac{1.0 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1.0 \text{ mol e}^-}{1.0 \text{ mol Na}} = 0.043 \text{ mol e}^-$	1 point is earned for the correct calculation of moles for Na
$\text{Ca, } 1.0 \text{ g Ca} \times \frac{1.0 \text{ mol Ca}}{40.08 \text{ g Ca}} \times \frac{2.0 \text{ mol e}^-}{1.0 \text{ mol Ca}} = 0.050 \text{ mol e}^-$	1 point is earned for taking 1 vs. 2 moles of electrons into account the correct answer.
The cell with the Ca anode would transfer more electrons.	

The only common oxide of zinc has the formula ZnO .

(i) Write the electron configuration for a Zn atom in the ground state.

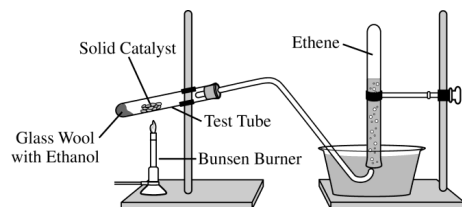
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ or $[\text{Ar}] 4s^2 3d^{10}$	1 point is earned for a correct configuration.
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(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

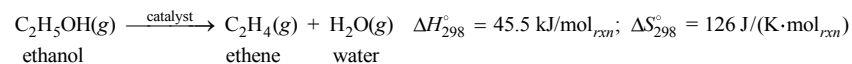
4s sublevel	1 point is earned for the correct answer.
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2015 SCORING GUIDELINES

Question



Ethene, $\text{C}_2\text{H}_4(\text{g})$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$ (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.



A student added a 0.200 g sample of $\text{C}_2\text{H}_5\text{OH}(\text{l})$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $\text{C}_2\text{H}_5\text{OH}(\text{l})$ evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. (The vapor pressure of water at 305 K is 35.7 torr.)

Calculate the number of moles of $\text{C}_2\text{H}_4(\text{g})$

(i) that are actually produced in the experiment and measured in the gas collection tube and

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

(ii) that would be produced if the dehydration reaction went to completion.

$0.200 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.1 \text{ g C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_5\text{OH}}$ $= 0.00434 \text{ mol C}_2\text{H}_4 \text{ produced}$	1 point is earned for the correct number of moles of ethene produced.
---	--

Calculate the percent yield of $\text{C}_2\text{H}_4(\text{g})$ in the experiment.

$\% \text{ yield} = \frac{\text{actual yield}}{\text{maximum possible yield}} \times 100 = \frac{0.00264 \text{ mol}}{0.00434 \text{ mol}} \times 100 = 60.8\%$	1 point is earned for the correct percent yield.
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2015 SCORING GUIDELINES

Question 2 (continued)

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of ΔG_{298}° for the reaction.

Yes, the data support the student's claim.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 45.5 \text{ kJ/mol}_{\text{rxn}} - (298 \text{ K})(0.126 \text{ kJ/(K}\cdot\text{mol}_{\text{rxn}})) = 8.0 \text{ kJ/mol}_{\text{rxn}}$$

Because $\Delta G^\circ > 0$, the value of $K_p = e^{\frac{-\Delta G^\circ}{RT}} < 1.00$.

1 point is earned for the correct calculation of Δ

1 point is earned for a valid justification.

The Lewis electron-dot diagram for C_2H_4 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for $\text{C}_2\text{H}_5\text{OH}$ by drawing in all of the electron pairs.

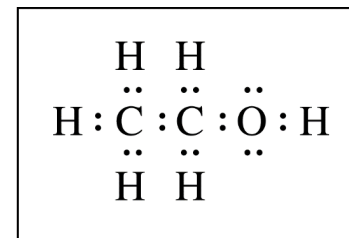
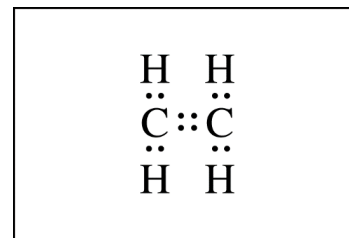


Diagram should include all bonding pairs plus two nonbonding pairs on the O atom. (A line may be used to represent an electron pair.)

1 point is earned for a correct diagram.

What is the approximate value of the C–O–H bond angle in the ethanol molecule?

The bond angle is approximately 109° .

1 point is earned for an angle from 100° to 115° .

2015 SCORING GUIDELINES

Question continued)

During the dehydration experiment, $\text{C}_2\text{H}_4(g)$ and unreacted $\text{C}_2\text{H}_5\text{OH}(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted $\text{C}_2\text{H}_5\text{OH}$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

Ethene is only slightly soluble in water because the weak dipole/induced dipole intermolecular attractions between nonpolar ethene molecules and polar water molecules are weaker than the hydrogen bonds between water molecules. Ethanol molecules are soluble in water because they are polar and form hydrogen bonds with water molecules as they dissolve.

1 point is earned for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of differences in polarity.

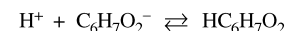
1 point is earned for describing the intermolecular forces between ethene and water as weak dipole/induced dipole forces and attributing the solubility of ethanol in water to the hydrogen bonds formed between ethanol molecules and water molecules.

2015 SCORING GUIDELINES

Question

Potassium sorbate, $\text{KC}_6\text{H}_7\text{O}_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $\text{KC}_6\text{H}_7\text{O}_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M $\text{HCl}(aq)$ using both an indicator and a pH meter. The value of K_a for sorbic acid, I_7O_2 , is 1.7×10^{-5} .

Write the net-ionic equation for the reaction between $\text{KC}_6\text{H}_7\text{O}_2(aq)$ and $\text{HCl}(aq)$.



1 point is earned the net-ionic equation.

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

$$\frac{1.25 \text{ mol HCl}}{1000 \text{ mL}} = \frac{x \text{ mol HCl}}{29.95 \text{ mL}} \quad x = 0.0374 \text{ mol HCl}$$

$$\frac{0.0374 \text{ mol C}_6\text{H}_7\text{O}_2^-}{45.0 \text{ mL}} = \frac{x \text{ mol C}_6\text{H}_7\text{O}_2^-}{1000 \text{ mL}} \Rightarrow 0.832 \text{ M}$$

1 point is earned for the moles of HCl at the equivalence point.

1 point is earned for the correct answer.

The pH at the equivalence point of the titration is measured to be 2.54. Which of the following indicators would be the best choice for determining the end point of the titration? Justify your answer.

Indicator	$\text{p}K_a$
Phenolphthalein	9.3
Bromothymol blue	7.0
Methyl red	5.0
Thymol blue	2.0
Methyl violet	0.80

Thymol blue; it has a $\text{p}K_a$ close to the pH at the equivalence point, so it will change color near the equivalence point.

1 point is earned for the correct indicator.

1 point is earned for correct justification.

Calculate the pH at the half-equivalence point.

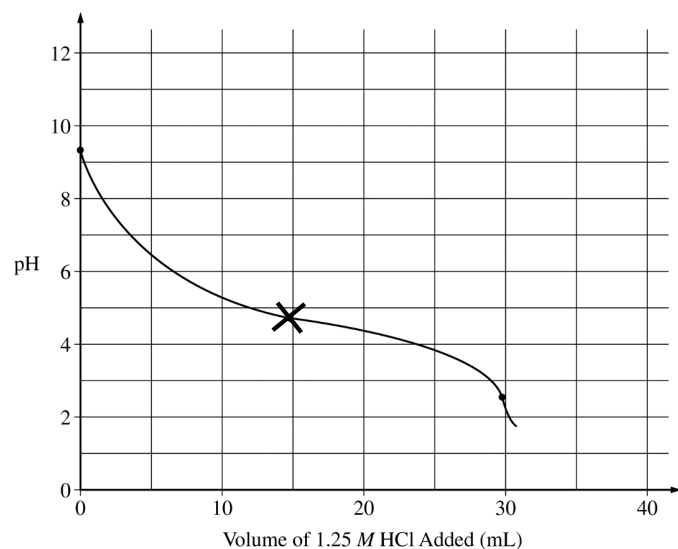
$$\text{pH} = \text{p}K_a = -\log(1.7 \times 10^{-5}) = 4.77$$

1 point is earned for the correct pH.

2015 SCORING GUIDELINES

Question 3 (continued)

The initial pH and the equivalence point are plotted on the graph below. Accurately sketch the titration curve on the graph below. Mark the position of the half-equivalence point on the curve with an



The pH curve should have the correct shape.]

- 1 point is earned for a half-equivalence point consistent with the answer to part (d) and at the correct volume.
- 1 point is earned for a curve that levels off to a relatively horizontal slope through the half-equivalence point.
- 1 point is earned for a relatively steep negative slope through the equivalence point.

2015 SCORING GUIDELINES

Question 3 (continued)

The pH of the soft drink is 3.37 after the addition of the $\text{KC}_6\text{H}_7\text{O}_2(aq)$. Which species, $\text{HC}_6\text{H}_7\text{O}_2$ or $\text{C}_6\text{H}_7\text{O}_2^-$, has a higher concentration in the soft drink? Justify your answer.

$$\text{For sorbic acid, } K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_7\text{O}_2^-]}{[\text{HC}_6\text{H}_7\text{O}_2]},$$

$$\text{thus } \frac{[\text{C}_6\text{H}_7\text{O}_2^-]}{[\text{HC}_6\text{H}_7\text{O}_2]} = \frac{K_a}{[\text{H}^+]} = \frac{1.7 \times 10^{-5}}{10^{-3.37}} \approx 0.04$$

$$\Rightarrow [\text{HC}_6\text{H}_7\text{O}_2] > [\text{C}_6\text{H}_7\text{O}_2^-]$$

The concentrations of $\text{HC}_6\text{H}_7\text{O}_2$ and $\text{C}_6\text{H}_7\text{O}_2^-$ are equal at the half-equivalence point. A pH of 3.37 is lower than that at the half-equivalence point, so the protonated form, $\text{HC}_6\text{H}_7\text{O}_2$, has a higher concentration in the soft drink.

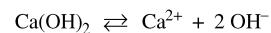
1 point is earned for identifying the correct species and for making a comparison involving the pH (with or without calculation).

2015 SCORING GUIDELINES

Question

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

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



1 point is earned for the correct equation.

Calculate the molar solubility of $\text{Ca}(\text{OH})_2$ in 0.10 M $\text{Ca}(\text{NO}_3)_2$.

$$= [\text{Ca}^{2+}] [\text{OH}^-]^2$$

$$: 10^{-6} = (0.10 + x) (2x)^2 \approx (0.10) 4x^2 \quad [\text{assuming } x \ll 0.10]$$

$$: 10^{-5} = 4x^2$$

$$= 0.0018 \text{ M}$$

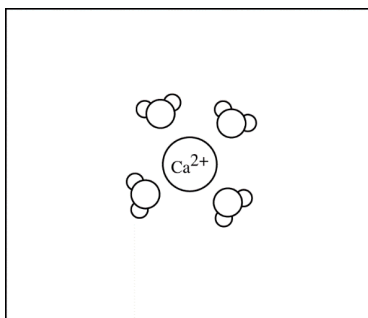
$$\text{Molar solubility of } \text{Ca}(\text{OH})_2 = 0.0018 \text{ M}$$

1 point is earned for the correct stoichiometry and setup.

1 point is earned for the final answer.

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

Represent water molecules as

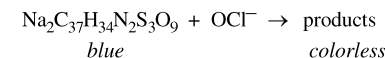


[The diagram should show the oxygen side of the water molecules oriented closer to the Ca^{2+} ion.]

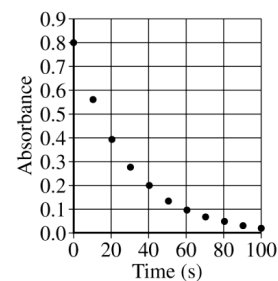
1 point is earned for a correct diagram that shows at least three of the four water molecules oriented as described.

2015 SCORING GUIDELINES

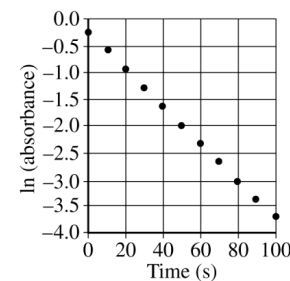
Question



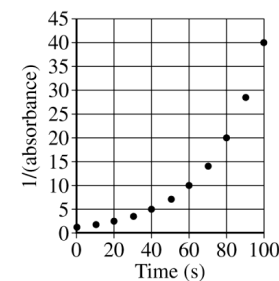
Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II



Graph III

Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?

First order

1 point is earned for the correct order.

The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.

- Increasing the temperature
- Increasing the concentration of the food coloring
- Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

2015 SCORING GUIDELINES

Question ntinued)

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

In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?

The spectrophotometer should be set to a different wavelength.	1 point is earned for a correct answer.
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2015 SCORING GUIDELINES

Question

Compound	Melting Point (°C)
LiI	449
KI	686
LiF	845
NaF	993

A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

Select two compounds from the table and explain how the data support the student's hypothesis.

LiI and KI. LiI has a small cation and a large anion and KI has a large cation and the same large anion. The melting point of LiI (with its smaller cation) is lower than that of KI.	1 point is earned for choosing an appropriate pair of compounds (LiI/KI, LiI/LiF, or LiI/NaF)
LiI and LiF. LiI has a small cation and a large anion and LiF has the same small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of LiF.	1 point is earned for an explanation that supports the hypothesis.
LiI and NaF. LiI has a small cation and a large anion and NaF has a relatively small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of NaF.	

Identify a compound from the table that can be dissolved in water to produce a basic solution. Write the net ionic equation for the reaction that occurs to cause the solution to be basic.

Either LiF or NaF is acceptable.	1 point is earned for choosing one of the correct compounds.
$+ \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$	1 point is earned for writing a correct balanced equation.

2015 SCORING GUIDELINES

Question

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

Calculate the amount of heat needed to purify 1.00 mole of Al originally at 298 K by melting it. The melting point of Al is 933 K. The molar heat capacity of Al is 24 J/(mol·K), and the heat of fusion of Al is 10.7 kJ/mol.

To raise the temperature from 298 K to 933 K:

$$= \frac{24 \text{ J}}{\text{mol K}} \times 1.00 \text{ mol} \times 635 \text{ K} = 15,000 \text{ J} = 15 \text{ kJ}$$

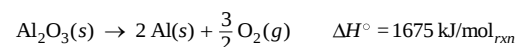
It takes 10.7 kJ to melt the Al at 933 K.

$$15 \text{ kJ} + 10.7 \text{ kJ} = 25.7 \text{ kJ}$$

1 point is earned for calculating the amount of heat needed to raise the temperature to 933 K.

1 point is earned for adding the heat of fusion to the previous result to get a final answer.

The equation for the overall process of extracting Al from Al_2O_3 is shown below. Which requires less energy, recycling existing Al or extracting Al from Al_2O_3 ? Justify your answer with a calculation.



For extracting Al from ore:

$$1675 \text{ kJ/mol}_{\text{rxn}} \times \frac{1 \text{ mol of reaction}}{2 \text{ mol Al}} = 837.5 \text{ kJ per mol of Al}$$

Producing 1.00 mol of Al from Al_2O_3 requires 837.5 kJ.

Because 26 kJ < 837.5 kJ, recycling requires less energy.

1 point is earned for a calculation to get equal numbers of moles for comparison.

1 point is earned for a correct comparison.

AP[®] Chemistry

2014 Scoring Guidelines

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4 SCORING GUIDELINES

Question 1
(10 points)

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

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

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

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

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

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

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

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

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

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

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

4 SCORING GUIDELINES

Question 1 (continued)

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

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

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

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

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

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

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

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

Yes. Addition of an excess of 0.20 M $AgNO_3(aq)$ will precipitate all of the I^- ion present in the solution because AgI is insoluble, as evidenced by its low value of K_{sp} .	1 point is earned for the correct answer with a valid justification.
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(ii) The student only has access to one KI tablet and a balance that can measure to the nearest 0.01 g. Will the student be able to determine the mass of AgI produced to three significant figures? Justify your answer.

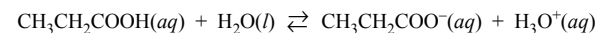
4 SCORING GUIDELINES

Question 1 (continued)

No. If masses can be measured to ± 0.01 g, then the mass of the dry AgI(s) precipitate (which is less than 1 g) will be known to only two significant figures.

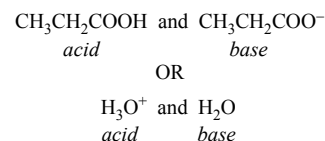
1 point is earned for a correct answer with a valid justification.

2014 SCORING GUIDELINES

Question
(10 points)

Propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 M $\text{CH}_3\text{CH}_2\text{COOH}$ is 2.79.

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



1 point is earned for writing (or naming) either of the Brønsted-Lowry conjugate acid-base pairs with a clear indication of which is the acid and which is the base.

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

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.79} = 1.6 \times 10^{-3} M$$

$$[\text{CH}_3\text{CH}_2\text{COO}^-] = [\text{H}_3\text{O}^+]$$

AND

$$[\text{CH}_3\text{CH}_2\text{COOH}] = 0.20 M - [\text{H}_3\text{O}^+], \text{ OR } [\text{CH}_3\text{CH}_2\text{COOH}] \approx 0.20 M$$

(state or assume that $[\text{H}_3\text{O}^+] \ll 0.20 M$)

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} = \frac{(1.6 \times 10^{-3} M)^2}{0.20 M} = 1.3 \times 10^{-5}$$

1 point is earned for correctly solving for $[\text{H}_3\text{O}^+]$.

1 point is earned for the K_a expression for propanoic acid
OR

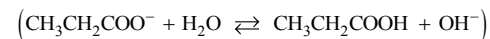
1 point is earned for substituting values into the K_a expression.

1 point is earned for correctly solving for the value of K_a .

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

- (i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 M $\text{CH}_3\text{CH}_2\text{COOH}$ with a 50.0 mL sample of 0.20 M NaOH is 7.00.

False. The conjugate base of a weak acid undergoes hydrolysis (see equation below) at equivalence to form a solution with a pH > 7 .



1 point is earned for noting that the statement is false AND providing a supporting explanation.

2014 SCORING GUIDELINES

Question 2 (continued)

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

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

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

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

Let x = moles of propanoic acid then $x = (0.02052 \text{ L NaOH}) \times \frac{0.173 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol acid}}{1 \text{ mol NaOH}}$ $= 3.55 \times 10^{-3} \text{ mol propanoic acid}$ $\frac{3.55 \times 10^{-3} \text{ mol acid}}{0.02500 \text{ L acid}} = 0.142 \text{ M}$ OR Since CH_3CH_2COOH is monoprotic and, at the equivalence point, moles $H^+ = \text{moles } OH^-$, then $M_A V_A = M_B V_B$ $M_A = \frac{M_B V_B}{V_A} = \frac{(0.173 \text{ M NaOH})(20.52 \text{ mL NaOH})}{25.00 \text{ mL acid}} = 0.142 \text{ M}$	1 point is earned for correctly calculating the number of moles of acid that reacted at the equivalence point. 1 point is earned for the correct molarity of acid.
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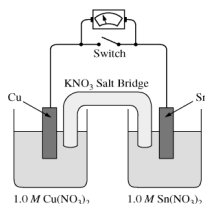
- (e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

2014 SCORING GUIDELINES

Question 2 (continued)

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

Question
(10 points)

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

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

Since the Sn electrode is losing mass, Sn atoms must be forming $\text{Sn}^{2+}(\text{aq})$. This process is oxidation.

OR

because the cell operates, E° must be positive and, based on the E° values from the table, it must be Sn that is oxidized.

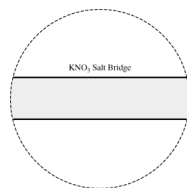
1 point is earned for the correct answer with justification.

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

The atoms on the Sn electrode are going into the solution as Sn^{2+} ions.

1 point is earned for the correct answer.

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



The response should show at least one K^+ ion moving toward the Cu compartment on the left and at least one NO_3^- ion moving in the opposite direction.

1 point is earned for correct representation of both K^+ and NO_3^- ions. (Including free electrons loses this point.)

1 point is earned for correctly indicating the direction of movement of both ions.

SCORING GUIDELINES

Question 3 (continued)

- (d) A nonstandard cell is made by replacing the 1.0 M solutions of $\text{Cu}(\text{NO}_3)_2$ and $\text{Sn}(\text{NO}_3)_2$ in the standard cell with 0.50 M solutions of $\text{Cu}(\text{NO}_3)_2$ and $\text{Sn}(\text{NO}_3)_2$. The volumes of solutions in the nonstandard cell are identical to those in the standard cell.

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

It is the same. In the cell reaction $Q = \frac{[\text{Sn}^{2+}]}{[\text{Cu}^{2+}]}$, and the concentrations of Sn^{2+} and Cu^{2+} are equal to each other in both cases.

1 point is earned for the correct answer with justification.

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

The nonstandard cell would power the device for a shorter time because the supply of Cu^{2+} ions will be exhausted more quickly.

OR

The nonstandard cell would power the device for a shorter time because the reaction will reach $E = 0$ more quickly.

1 point is earned for the correct answer with justification.

- (e) In another experiment, the student places a new Sn electrode into a fresh solution of 1.0 M $\text{Cu}(\text{NO}_3)_2$.

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

- (i) Using information from the table above, write a net-ionic equation for the reaction between the Sn electrode and the $\text{Cu}(\text{NO}_3)_2$ solution that would be thermodynamically favorable. Justify that the reaction is thermodynamically favorable.

SCORING GUIDELINES

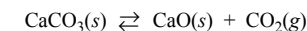
Question 3 (continued)

$\text{Cu}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Sn}^{2+}(\text{aq})$ E° is positive ($0.34 \text{ V} + 0.14 \text{ V} = 0.48 \text{ V}$), therefore the reaction is thermodynamically favorable. OR The cell observations from earlier parts of the question are evidence that the Sn is oxidized and Cu is reduced, therefore E° must be positive.	1 point is earned for the correct net-ionic equation. 1 point is earned for a correct justification (unit not needed in calculation).
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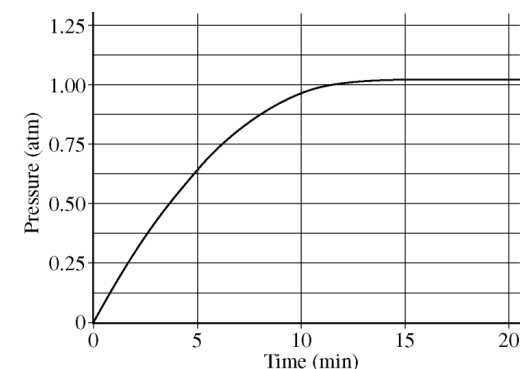
(ii) Calculate the value of ΔG° for the reaction. Include units with your answer.

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

SCORING GUIDELINES

Question
(4 points)

When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(\text{s})$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(\text{g})$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(\text{s})$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

(a) Calculate the number of moles of $\text{CO}_2(\text{g})$ present in the container after 20 minutes of heating.

$PV = nRT$ $\frac{PV}{RT} = n = \frac{(1.04 \text{ atm})(1.00 \text{ L})}{(0.0821 \frac{\text{L atm}}{\text{mol K}})(1100 \text{ K})} = 0.0115 \text{ mol CO}_2$	1 point is earned for the proper setup using the ideal gas law and an answer that is consistent with the setup.
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SCORING GUIDELINES

Question continued)

- (b) The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.

Do not agree with claim Explanation I: In experiment 1, the moles of $\text{CaCO}_3 = 50.0 \text{ g}/100.09 \text{ g/mol} = 0.500 \text{ mol CaCO}_3$. If the reaction had gone to completion, 0.500 mol of CO_2 would have been produced. From part (a) only 0.0115 mol was produced. Hence, the student's claim was false. Explanation II: The two different experiments (one with 50.0 g of CaCO_3 and one with 100.0 g of CaCO_3) reached the same constant, final pressure of 1.04 atm. Since increasing the amount of reactant did not produce more product, there is no way that all of the CaCO_3 reacted. Instead, an equilibrium condition has been achieved and there must be some solid CaCO_3 in the container.	1 point is earned for disagreement with the claim <u>and</u> for a correct justification using stoichiometry or a discussion of the creation of an equilibrium condition.
--	--

- (c) After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

The final pressure would be equal to 1.04 atm. Equilibrium was reached in both experiments; the equilibrium pressure at this temperature is 1.04 atm. As the reaction shifts toward the reactant, the amount of $\text{CO}_2(g)$ in the container will decrease until the pressure returns to 1.04 atm.	1 point is earned for the correct answer with justification.
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- (d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.

SCORING GUIDELINES

Question continued)

Yes. For the equilibrium reaction represented by the chemical equation in this problem, at a given temperature the equilibrium pressure of CO_2 determines the equilibrium constant. Since the measured pressure of CO_2 is also the equilibrium pressure of CO_2 , $K_p = P_{\text{CO}_2} = 1.04$.

Note: If the response in part (b) indicates “yes”, that all of the $\text{CaCO}_3(s)$ had decomposed, then the point can be earned by stating that the system did not reach equilibrium in either experiment and hence the value of K_p cannot be calculated from the data.

1 point is earned for correct explanation that is consistent with the student's answer to part (b).

SCORING GUIDELINES

Question 5
(4 points)

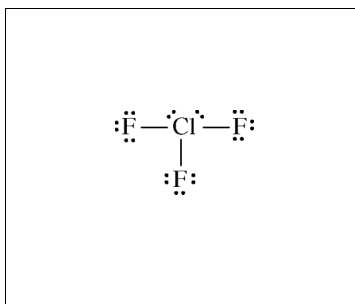
Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF ₄	NF ₃	OF ₂	No compound	SiF ₄	PF ₃	SF ₂	No compound

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

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

ClF	1 point is earned for the correct formula.
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- (b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF₃. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF₃.



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

Question 5 (continued)

- (c) Two possible geometric shapes for the ClF₃ molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF₃ molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

The molecule is T-shaped because a T-shaped structure is asymmetric with dipoles that do not cancel out, but produce a net dipole (i.e., a polar molecule). OR because, if the molecule had a trigonal planar structure, the molecule would be symmetric with dipoles that cancel out and produce a net dipole of zero (i.e., a nonpolar molecule), which is not consistent with the observation that the ClF₃ molecule does have a dipole moment.	1 point is earned for indicating that the molecule is T-shaped with an acceptable explanation.
---	--

In an attempt to resolve the existence of the ClF₃ molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

Halogen	Formula(s)
F	F ₂
Cl	
Br	BrF, BrF ₃ , BrF ₅
I	IF, IF ₃ , IF ₅ , IF ₇

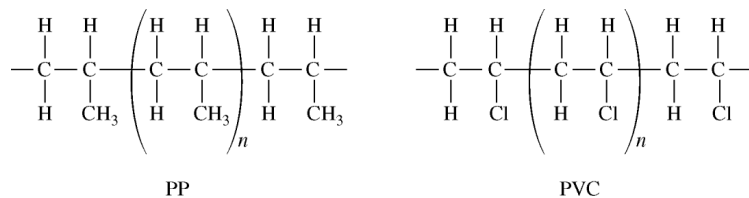
- (d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

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

Question
(4 points)

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

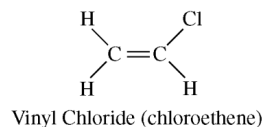
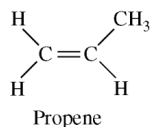


- (a) Given that the spacing between polymer chains in PP and PVC is similar, the beads that sink are made of which polymer? Explain.

The PVC beads sink. The spacing between chains is similar, but a Cl atom has a greater mass than CH₃.

1 point is earned for the correct polymer with a correct explanation.

PP is synthesized from propene, C₃H₆, and PVC is synthesized from vinyl chloride, C₂H₃Cl. The structures of the molecules are shown below.



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

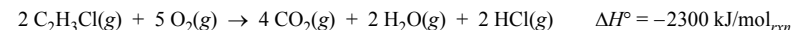
Both substances have dipole-dipole interactions and London dispersion forces (or propene is essentially nonpolar with only LDFs while vinyl chloride has both LDFs and dipole-dipole forces). Propene contains a CH₃ group, but vinyl chloride contains a Cl atom. Vinyl chloride thus has a larger electron cloud, is more polarizable, and has a larger dipole moment. Thus intermolecular attractions are stronger in vinyl chloride, which results in it having the higher boiling point.

1 point is earned for a discussion of intermolecular forces and for a comparison of their relative strengths.

SCORING GUIDELINES

Question 6 (continued)

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



- (c) Using the table of standard enthalpies of formation below, determine whether the combustion of 2.00 mol of propene releases more, less, or the same amount of energy that 2.00 mol of vinyl chloride releases. Justify your answer with a calculation. The balanced equation for the combustion of 2.00 mol of propene is $2 \text{C}_3\text{H}_6(g) + 9 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g)$.

Substance	C ₂ H ₃ Cl(g)	C ₃ H ₆ (g)	CO ₂ (g)	H ₂ O(g)	HCl(g)	O ₂ (g)
Standard Enthalpy of Formation (kJ/mol)	37	21	−394	−242	−92	0

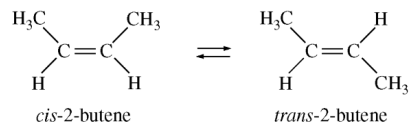
$$\Delta H^\circ = 6(-394) + 6(-242) - 2(21) = -3858 \text{ kJ/mol}_{\text{rxn}}$$

The combustion of 2.00 mol of propene releases more energy.

1 point is earned for the calculation of the enthalpy of combustion of propene.

1 point is earned for the comparison of propene to vinyl chloride that is consistent with the calculated value.

SCORING GUIDELINES

Question 7
(4 points)

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

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

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

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

1 point is earned for a correct explanation.

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

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100. \text{ s}} = 0.00693 \text{ s}^{-1}$$

1 point is earned for correct numerical answer with units.

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

The initial rate in trial 1 is less than that in trial 2 because $\text{rate} = k[\text{cis-2-butene}]$ or $\text{rate} = kP_{\text{cis-2-butene}}$ (with reference to values from both trials).

OR

because the initial concentration of *cis*-2-butene in trial 1 is less than that in trial 2 and k is constant.

1 point is earned for the correct answer with justification.

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

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

1 point is earned for a correct answer with justification.