Question 7: Short Answer **4 points**

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

$$0.1000 \text{ L} \times \frac{0.340 \text{ mol}}{1 \text{ L}} \times \frac{58.44 \text{ g}}{1 \text{ mol}} = 1.99 \text{ g NaCl}$$

(b) For a correct description of step 2: **1 point**

Combine the solid NaCl *and some distilled water in a* 100.0 mL *volumetric flask.*

For a correct description of step 4: **1 point**

Fill the volumetric flask with distilled water to the calibration (100.0 mL) *mark.*

Total for part (b) 2 points

(c) For the correct prediction and a valid explanation: **1 point**

It would decrease. The solvent front will not travel as far in the second experiment, so the separation will be smaller.

Total for question 7 4 points

Question 3: Long Answer — 10 points

(a) For a correct electron configuration: **1 point**

Accept one of the following:

- $1s^2 2s^2 2p^6 3s^2 3p^1$
- $[Ne]\ 3s^2 3p^1$

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

The highest occupied electron shell (n=3) of Al *is at a greater average distance from the nucleus than the highest occupied electron shell (n=2) of* Al^{3+}.

(c) For the correct steps to dissolve the solute in water (steps may be consolidated): **1 point**

2. Partially fill the volumetric flask with some distilled water

3. Add the weighed $AgNO_3(s)$ *to the volumetric flask*

4. Swirl to dissolve the solid

For the correct step to ensure quantitative dilution: **1 point**

*5. After the solid is dissolved, fill the flask to the calibration (*200.00 mL*) mark and mix.*

Total for part (c) 2 points

(d) For a drawing that shows product formation and indicates the conservation of matter: **1 point**

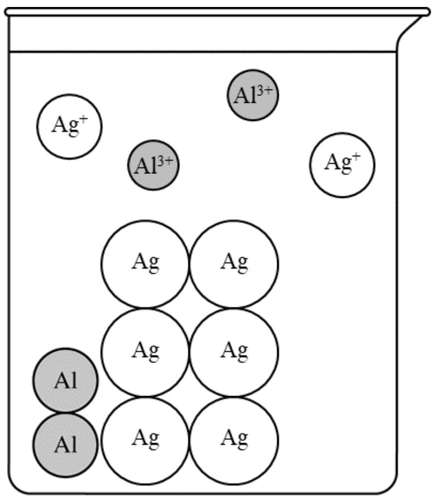
4 Al *and* 8 Ag *particles in the beaker on right (see sample drawing below)*

For a drawing that shows product formation and conservation of charge: **1 point**

2 Ag^+ *ions and* 2 Al^{3+} *ions in the beaker on the right (see sample drawing below)*

For a drawing that shows product formation and correct phases of matter for all species: **1 point**

6 Ag *atoms that are solid and* 2 Al^{3+} *ions that are aqueous in the beaker on the right*



Total for part (d) 3 points

(e)	For the correct calculated value: Accept one of the following: • $E° = 0.80 \text{ V} + 1.66 \text{ V} = 2.46 \text{ V}$ • $E^{\circ}_{cell} = E^{\circ}_{red} - E^{\circ}_{ox} = 0.80 \text{ V} - (-1.66 \text{ V}) = 2.46 \text{ V}$	**1 point**
(f)	For the correct answer and a valid justification: *Negative. The reaction has a positive value of* $E°$*, indicating that it is thermodynamically favorable and would therefore have a negative value of* $\Delta G°$*. (*$\Delta G° = -nFE°$*)*	**1 point**
(g)	For the correct answer and a valid justification: Accept one of the following: • *Zero. The observation that the reaction stops progressing implies that* $E_{cell} = 0$*, indicating that there is no longer a driving force for the reaction.* • *Zero. The observation that reaction stops progressing implies that equilibrium is established, and* $\Delta G = 0$ *at equilibrium.*	**1 point**
	Total for question 3	**10 points**

Question 6: Short Answer — 4 points

(a)	For the correct answer: 525 nm	**1 point**
(b)(i)	For the correct answer: 92.0 mL	**1 point**
(ii)	For the correct calculated value: $V_1 = \frac{M_2V_2}{M_1} = \frac{(1.68 \times 10^{-3}\ M)(100.0 \text{ mL})}{(2.40 \times 10^{-3}\ M)} = 70.0 \text{ mL}$	**1 point**
	Total for part (b)	**2 points**
(c)	For the correct answer and a valid justification: *The student could have improperly executed step 3. If the cuvette was not rinsed with the standard solution prior to being filled for the measurement of absorbance, the standard solution would be diluted by the remaining distilled water, and the absorbance would be lower than what it should be.*	**1 point**
	Total for question 6	**4 points**

Question 3: Long Answer — 10 points

(a)	For the correct balanced equation (state symbols not required): $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$	**1 point**
(b)	For the correct calculated value of the mass of precipitate (may be implicit): $1.136 \text{ g} - 0.764 \text{ g} = 0.372 \text{ g } BaSO_4$	**1 point**
	For the correct calculated value of the number of moles, consistent with mass of precipitate: $0.372 \text{ g} \times \frac{1 \text{ mol}}{233.39 \text{ g}} = 0.00159 \text{ mol}$	**1 point**
	Total for part (b)	**2 points**
(c)	For the correct calculated value, consistent with part (b): $0.00159 \text{ mol } BaSO_4 \times \frac{1 \text{ mol } CuSO_4}{1 \text{ mol } BaSO_4} = 0.00159 \text{ mol } CuSO_4$ $\frac{0.00159 \text{ mol } CuSO_4}{0.0500 \text{ L}} = 0.0318\ M\ CuSO_4$ *(0.0319 M if decimals are carried)*	**1 point**
(d)	For the correct calculated value: $M_1V_1 = M_2V_2$ $V_1 = \frac{(0.0500\ M)(50.00 \text{ mL})}{(0.1000\ M)} = 25.0 \text{ mL}$	**1 point**
(e)	For a correct technique to measure the volume of solution: *First, measure out the correct volume of 0.1000 M $CuSO_4$ solution with a 25.0 mL volumetric pipet (graduated cylinder or buret is acceptable).*	**1 point**
	For a correct technique to dilute the solution to the final volume: *Transfer the 25.0 mL of solution to a 50.00 mL volumetric flask and dilute the solution with water up to the 50.00 mL mark.*	**1 point**
	Total for part (e)	**2 points**
(f)	For the correct value (between 0.032 *M* and 0.038 *M*): Accept one of the following: • $y = mx = \frac{0.63}{0.1000}x = 6.3x$ $x = \frac{y}{6.3} = \frac{0.219\ M}{6.3} = 0.035\ M$ • *Estimated value from the graph within the specified range.*	**1 point**

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

The concentration will be <u>less than</u> that determined in part (f).

For a valid justification: **1 point**

The additional water will decrease the concentration of $CuSO_4$ in the cuvette. Therefore, there will be a decrease in absorbance (according to the Beer-Lambert law). This dilution results in a lower estimated concentration of $CuSO_4$.

Total for part (g) 2 points

Total for question 3 10 points

Question 6: Short Answer 4 points

(a) For a correct description: **1 point**

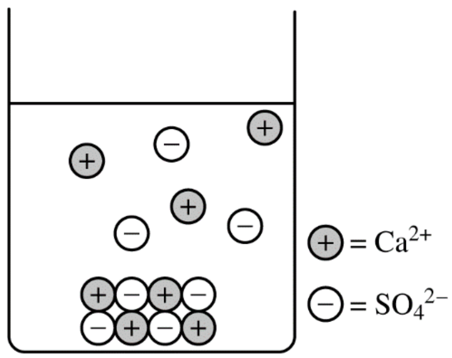
Ionic solids do not have free-moving ions that are required to carry an electric current. Therefore, there is no conduction of electricity.

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

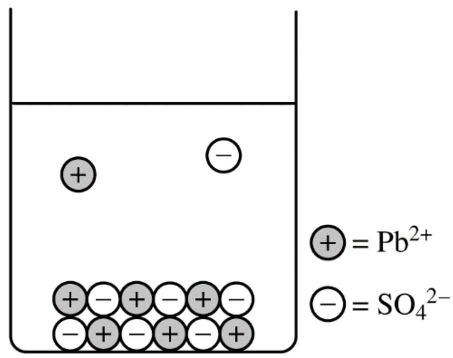
$CaSO_4$. The greater electrical conductivity of the $CaSO_4$ solution relative to the $PbSO_4$ solution implies a higher concentration of ions, which comes from the dissolution (dissociation) of $CaSO_4$ to a greater extent.

(c) For a correct drawing that shows an equal number of cations and anions: **1 point**

The drawing shows solid $PbSO_4$ at the bottom of the beaker (similar to the solid shown for $CaSO_4$) and fewer dissociated Pb^{2+} and SO_4^{2-} ions in the solution.



Higher Conductivity Solution



Lower Conductivity Solution

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

The additional precipitate is $CaSO_4$ that forms in response to the increased $[SO_4^{2-}]$ in solution. According to Le Chatelier's principle ($Q > K_{sp}$), the introduction of SO_4^{2-} as a common ion shifts the equilibrium towards the formation of more $CaSO_4(s)$.

Total for question 6 4 points

2019

AP CollegeBoard

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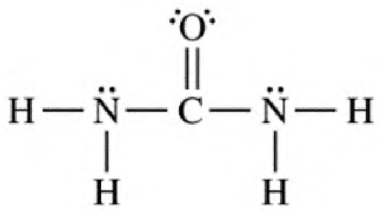
Scoring Guidelines

2019 SCORING GUIDELINES

Question 1

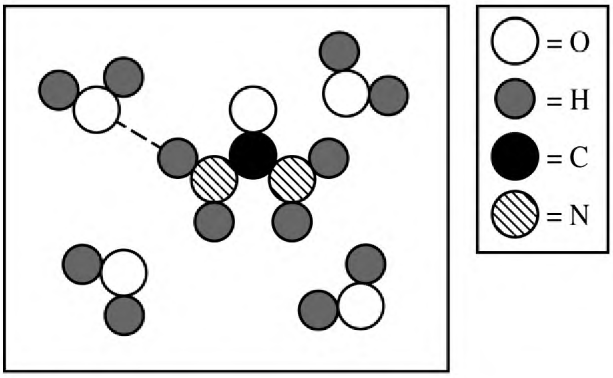


The compound urea, H_2NCONH_2, is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(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.

(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.

$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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.

2019 SCORING GUIDELINES

Question 1 (continued)

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

$5.39 \text{ g } H_2NCONH_2 \times \frac{1 \text{ mol}}{60.06 \text{ g}} = 0.0897 \text{ mol}$ $\frac{0.0897 \text{ mol}}{0.00500 \text{ L}} = 17.9\ M$	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.

2019 SCORING GUIDELINES

Question 1 (continued)

	$S°$ (J/(mol·K))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, $\Delta S°_{soln}$, 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.

$\Delta S°_{soln} = S°(H_2NCONH_2(aq)) - S°(H_2NCONH_2(s))$ $70.1\text{ J/(mol·K)} = S°(H_2NCONH_2(aq)) - 104.6\text{ J/(mol·K)}$ $S°(H_2NCONH_2(aq)) = 174.7\text{ J/(mol·K)}$	1 point is earned for the correct answer.

(g) Using particle-level reasoning, explain why $\Delta S°_{soln}$ 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 $\Delta S°_{soln}$.	1 point is earned for a correct explanation.

(h) The student claims that $\Delta S°$ 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 $\Delta G°$, with $\Delta G° = \Delta H° - T\Delta S°$. Since $\Delta S°$ is positive, the $T\Delta S°$ term makes the value of $\Delta G°$ smaller and thus makes the dissolution more thermodynamically favorable.	1 point is earned for the correct answer.

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.

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: NaBr(*aq*), $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	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.

$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$ $E° = E°(\text{reduced species}) - E°(\text{oxidized species})$ $= 1.36\text{ V} - 1.07\text{ V} = +0.29\text{ V}$. 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 $E°$.

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 <u>each</u> substance.

2019 SCORING GUIDELINES

Question 2 (continued)

The only intermolecular attractions in $Br_2(l)$ are London forces, while those in $BrCl(l)$ 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 $Br_2(l)$ are stronger than the combined intermolecular forces in $BrCl(l)$. Thus, the boiling point of $Br_2(l)$ is greater than that of $BrCl(l)$.	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.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H^\circ = 1.6 \text{ kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ 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.

$K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$ or $K_{eq} = \frac{P_{Br_2} P_{Cl_2}}{(P_{BrCl})^2}$	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.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g)$$

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

1 point is earned for correct stoichiometric values at equilibrium.

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

$2x$ = 0.51 atm ⟹ $x = 0.26$ atm

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

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

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

2019 SCORING GUIDELINES

Question 2 (continued)

Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol
nformation in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

$\Delta \quad = \sum$ (bond energies)$_{broken}$ – $\sum$ (bond energies)$_{formed}$ J/mol = 2(Br–Cl bond energy) – (193 kJ/mol + 243 kJ/mol) ·36 + 1.6) kJ/mol = 2(Br–Cl bond energy) Cl bond energy = 219 kJ/mol	1 point is earned for a correct calculation of the Br–Cl bond energy.

2019 SCORING GUIDELINES

Question 3

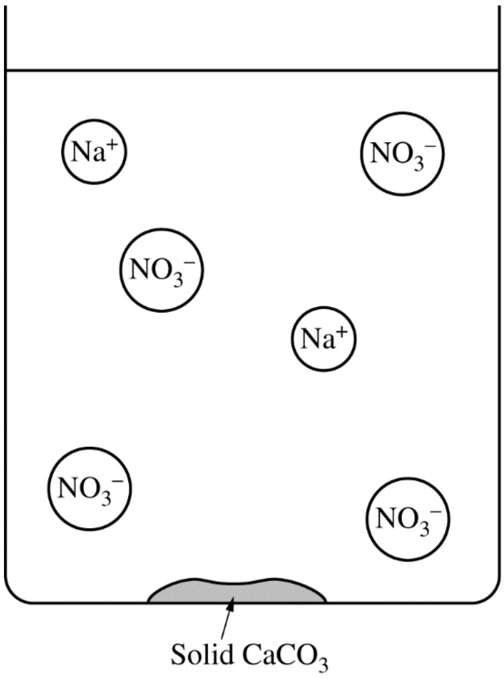
A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and Ca(NO mixed.

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$	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.

2019 SCORING GUIDELINES

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* $Ca(NO_3)_2$ 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.

$0.93 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g}} = 0.0093 \text{ mol } CaCO_3$ $0.0093 \text{ mol } CaCO_3 \times \frac{1 \text{ mol } Na_2CO_3}{1 \text{ mol } CaCO_3} = 0.0093 \text{ mol } Na_2CO_3$	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 $Na_2CO_3(aq)$ 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 ($Na^+(aq)$, (aq), and $NO_3^-(aq)$) 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 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \quad 10^{4}$$

2019 SCORING GUIDELINES

Question 3 (continued)

The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

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

Determine the pH of the solution using a pH meter.	1 point is earned for identifying a valid method.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

First determine $[OH^-]$ using pOH = 14 – pH, then $[OH^-] = 10^{-pOH}$. use the K_b expression and an ICE table (see example below) to determine $[CO_3^{2-}]$ and $[HCO_3^-]$ 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^-.	1 point is earned for a valid method of determining $[OH^-$ from the measured value.
(see ICE table and equation below)	1 point is earned for a valid method of determining the <u>initial</u> concentration of CO_3^{2-}.

	$CO_3^{2-}(aq)$	+ $H_2O(l)$	$\rightleftarrows$	$HCO_3^-(aq)$	+ $OH^-(aq)$
	c_i	---		0	0
	$-x$	---		$+x$	$+x$
	$c_i - x$	---		x	x

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

In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

Less than. The small value of K_b, 2.1×10^{-4}, indicates he reactants are favored.	1 point is earned for the correct answer with a valid justification.

The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

he Na_2CO_3 solution is not suitable. The pK_a of HCO_3^- is 10.32. Buffers are effective when the required pH is approximately equal to the pK_a of the weak acid. An acid with a pK_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.

2019 SCORING GUIDELINES

Question 4

dent is doing experiments with $CO_2(g)$. 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 $CO_2(g)$ in the container to 425 K.

Describe the effect of raising the temperature on the motion of the $CO_2(g)$ molecules.

e average speed of the molecules increases as temperature increases.	1 point is earned for the correct answer.

Calculate the pressure of the $CO_2(g)$ in the container at 425 K.

Both the volume and the number of molecules are constant, therefore $\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \Rightarrow \quad \frac{0.70\text{ atm}}{299\text{ K}} = \frac{P_2}{425\text{ K}} \quad \Rightarrow \quad P_2 = 0.99\text{ atm}$	1 point is earned for the correct answer.

In terms of kinetic molecular theory, briefly explain why the pressure of the $CO_2(g)$ 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. ster-moving gas particles collide more forcefully with the walls of the container, thus increasing the pressure.	1 point is earned for a correct explanation.

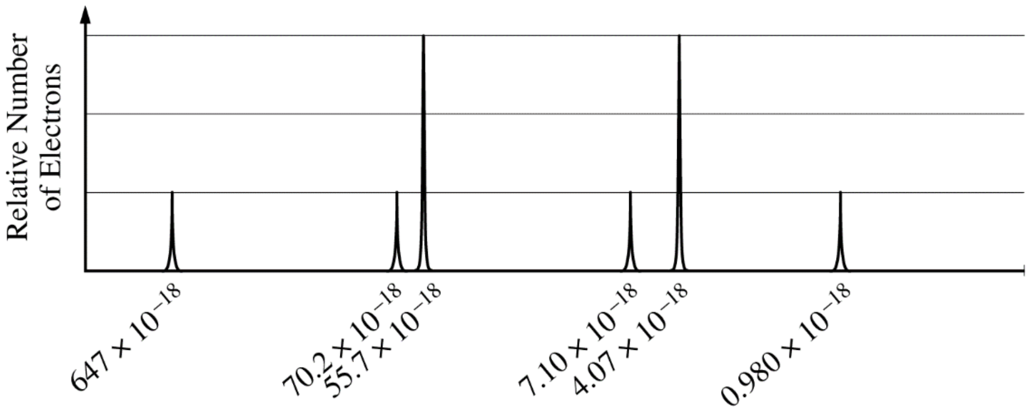
The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

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.

2019 SCORING GUIDELINES

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 $[Ar]\ 4s^2$	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 = 0.980×10^{-18} J $E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$ $\lambda = \frac{(6.626 \times 10^{-34}\ \mathrm{J\,s})(2.998 \times 10^{8}\ \mathrm{m\,s^{-1}})}{0.980 \times 10^{-18}\ \mathrm{J}}$ $\lambda = 2.03 \times 10^{-7}$ 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.

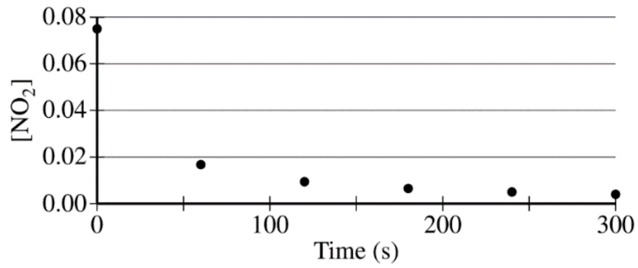
2019 SCORING GUIDELINES

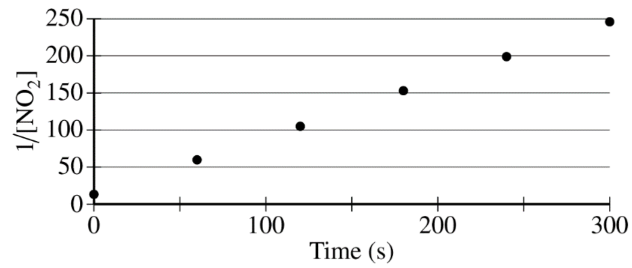
Question 6

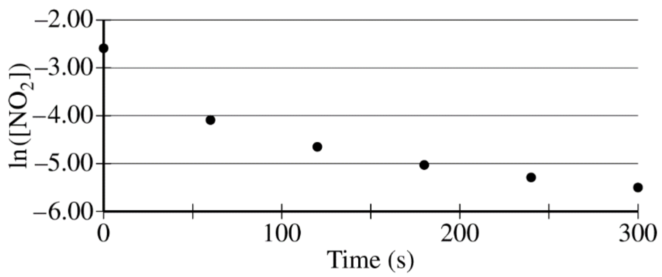
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

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

The concentration of a sample of $NO_2(g)$ 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 $\dfrac{1}{[NO_2]}$ 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 $NO_2(g)$.

rate = $k[NO_2]^2$	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:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[NO_2][NO_2] = k[NO_2]^2$, 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 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[N_2O_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$ in step 1, $[N_2O_4] = K_{eq}[NO_2]^2$. Then, substituting $K_{eq}[NO_2]^2$ for $[N_2O_4]$ in the rate law of step 2 gives rate = $(k\ K_{eq})[NO_2]^2$, 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

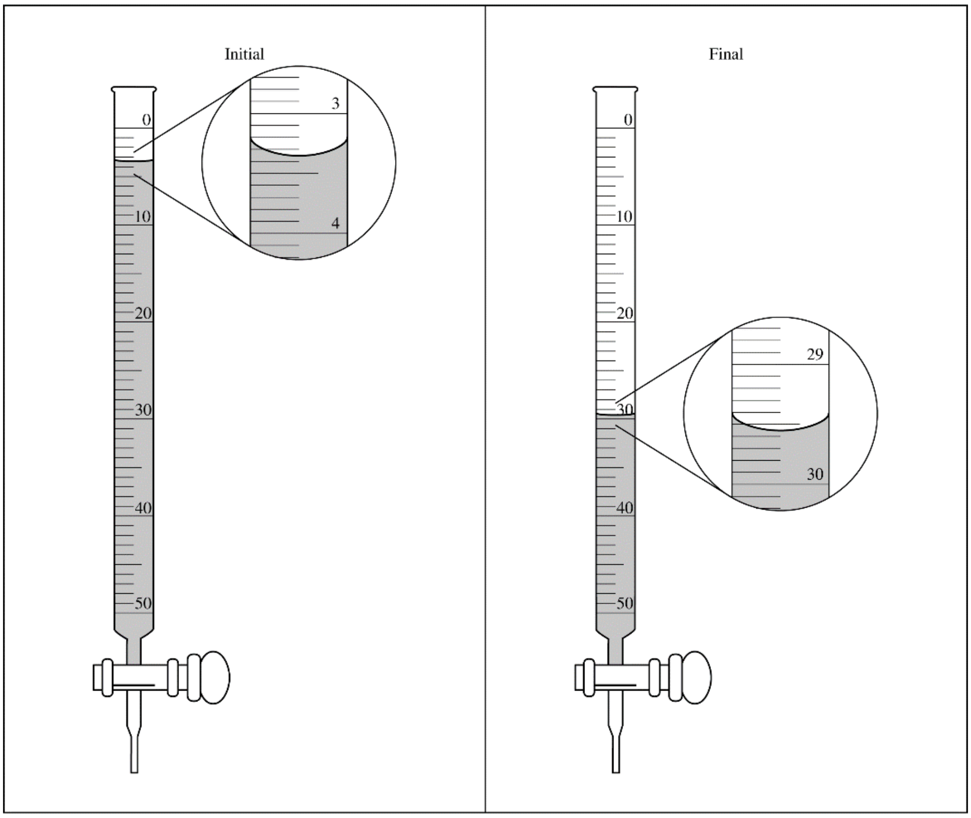
$$6\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) \rightarrow 10\ CO_2(g) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$$

A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ 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 $KMnO_4(aq)$ to the $H_2C_2O_4(aq)$ 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 $KMnO_4(aq)$ that was added during the titration.



29.55 mL − 3.35 mL = 26.20 mL	1 point is earned for the correct answer.

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Question 7 (continued)

Given that the concentration of $KMnO_4(aq)$ was 0.0235 M, calculate the number of moles of MnO^- ions that completely reacted with the $H_2C_2O_4$.

(0.02620 L)(0.0235 mol/L) = 0.000616 mol	1 point is earned for the correct answer.

The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 M $KMnO_4(aq)$ 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 olume 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.

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2015 Scoring Guidelines

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)
$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$	+0.34
$ZnO(s) + H_2O(l) + 2\ e^- \rightarrow Zn(s) + 2\ OH^-(aq)$	−1.31
$Na_2O(s) + H_2O(l) + 2\ e^- \rightarrow 2\ Na(s) + 2\ OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\ e^- \rightarrow Ca(s) + 2\ OH^-(aq)$	−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.

$$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$$

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

$E_{cell} = 0.34\ V - (-1.31\ V) = 1.65\ V$	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.

(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 $Zn(s)$ in the cell, producing $ZnO(s)$, which has more mass than the original $Zn(s)$.	1 point is earned for the justification.

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.

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

$O_2(g)$, 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.

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

The only common oxide of zinc has the formula ZnO.

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

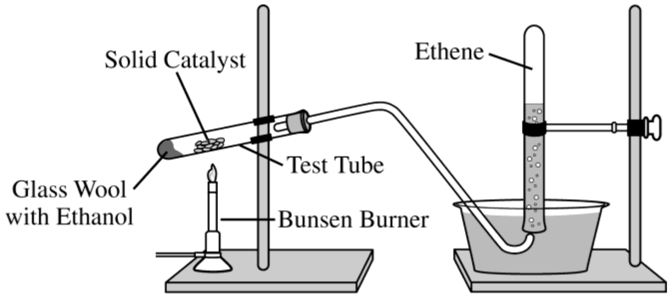
$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2\ 3d^{10}$ or $[\text{Ar}]\ 4s^2\ 3d^{10}$	1 point is earned for a correct configuration.

(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.

2015 SCORING GUIDELINES

Question



Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH($ (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.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{rxn};\ \Delta S^\circ_{298} = 126 \text{ J/(K·mol}_{rxn})$$

A student added a 0.200 g sample of $C_2H_5OH(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $C_2H_5OH(l)$ 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 $C_2H_4(g)$

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

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

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

$0.200 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.1 \text{ g } C_2H_5OH} \times \frac{1 \text{ mol } C_2H_4}{1 \text{ mol } C_2H_5OH}$ $= 0.00434 \text{ mol } C_2H_4$ produced	1 point is earned for the correct number of moles of ethene produced.

Calculate the percent yield of $C_2H_4(g)$ 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.

2015 SCORING GUIDELINES

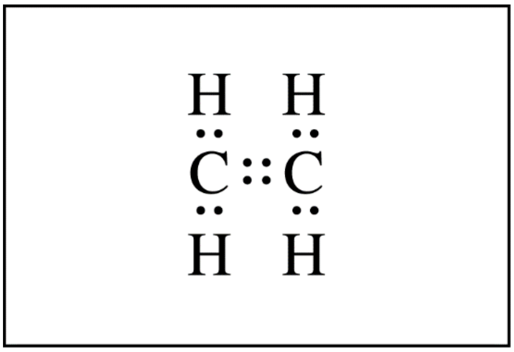
Question 2 (continued)

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. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= 45.5\ \text{kJ/mol}_{rxn} - (298\ \text{K})(0.126\ \text{kJ/(K}\cdot\text{mol}_{rxn}\text{)}) = 8.0\ \text{kJ/mol}_{rxn}$:ause $\Delta G^\circ > 0$, 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 C_2H_5OH by drawing in all of the electron pairs.



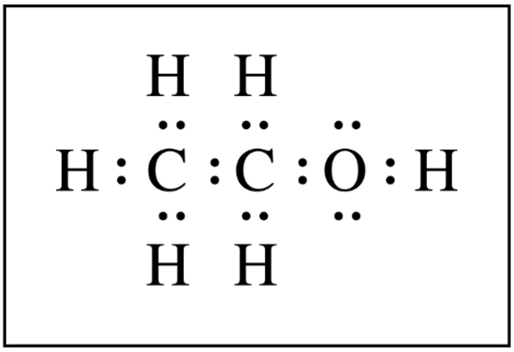


Diagram should include all bonding pairs plus two nonbonding pairs on the O atom. (A line may be used to represent an electron pair.)	1 point is earned for a correct diagram.

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, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH 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, $KC_6H_7O_2$ (molar mass 150. g/mol) is commonly added to diet soft drinks as a preservative. A stock solution of $KC_6H_7O_2(aq)$ of known concentration must be prepared. A student titrates 45.00 mL of the stock solution with 1.25 M 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 $KC_6H_7O_2(aq)$ and HCl(aq).

$H^+ + C_6H_7O_2^- \rightleftarrows HC_6H_7O_2$	1 point is earned the net-ionic equation.

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

$\frac{1.25 \text{ mol HCl}}{1000 \text{ mL}} = \frac{x \text{ mol HCl}}{29.95 \text{ mL}}$ $x = 0.0374$ mol HCl	1 point is earned for the moles of HCl at the equivalence point.
$\frac{0.0374 \text{ mol } C_6H_7O_2^-}{45.0 \text{ mL}} = \frac{x \text{ mol } C_6H_7O_2^-}{1000 \text{ mL}} \Rightarrow 0.832\ M$	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	pK_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 pK_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.

$pH = pK_a = -\log(1.7 \times 10^{-5}) = 4.77$	1 point is earned for the correct pH.

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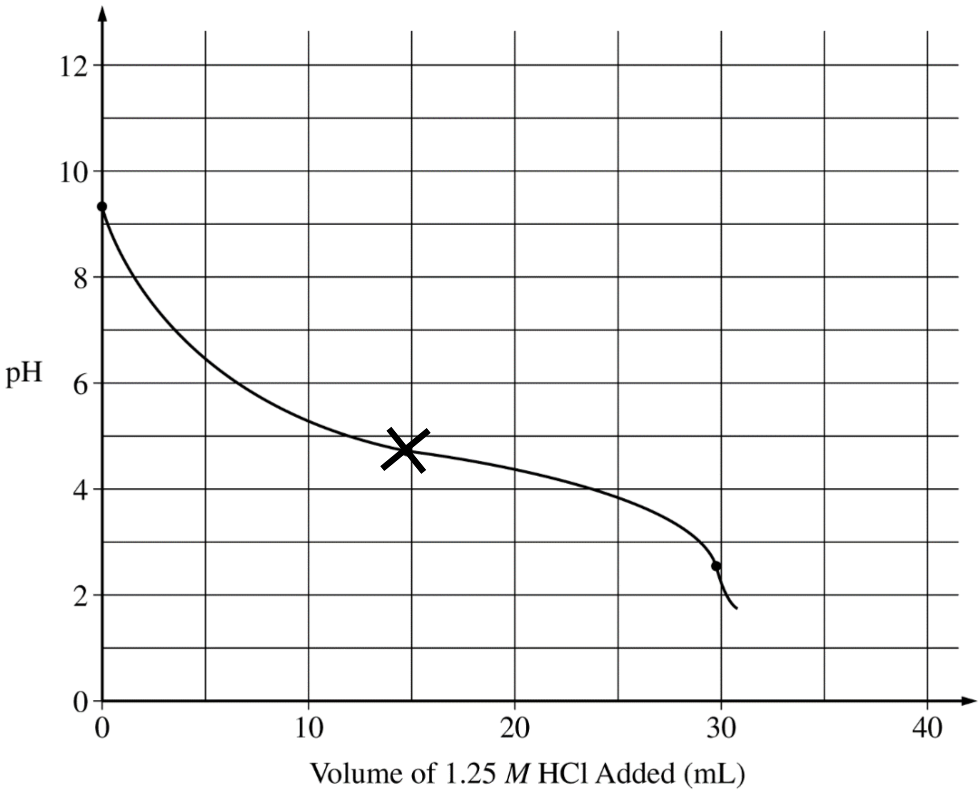
Question 3 (continued)

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



he 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.

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Question 3 (continued)

The pH of the soft drink is 3.37 after the addition of the $KC_6H_7O_2(aq)$. Which species, $HC_6H_7O_2$ $H_7O_2^-$, has a higher concentration in the soft drink? Justify your answer.

For sorbic acid, $K_a = \dfrac{[H^+][C_6H_7O_2^-]}{[HC_6H_7O_2]}$, thus $\dfrac{[C_6H_7O_2^-]}{[HC_6H_7O_2]} = \dfrac{K_a}{[H^+]} = \dfrac{1.7 \times 10^{-5}}{10^{-3.37}} \approx 0.04$ $\Rightarrow\ [HC_6H_7O_2] > [C_6H_7O_2^-]$ The concentrations of $HC_6H_7O_2$ and $C_6H_7O_2^-$ 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, H_7O_2, has a higher concentration in the soft drink.	1 point is earned for identifying the correct species <u>and</u> for making a comparison involving the pH (with or without calculation).

2015 SCORING GUIDELINES

Question

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

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

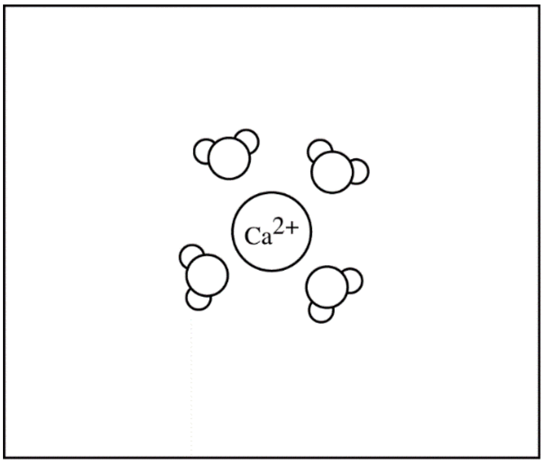
$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2\ OH^-$	1 point is earned for the correct equation.

Calculate the molar solubility of $Ca(OH)_2$ in 0.10 M $Ca(NO_3)_2$.

$= [Ca^{2+}]\ [OH^-]^2$: $10^{-6} = (0.10 + x)\ (2x)^2 \approx (0.10)\ 4x^2$ [assuming $x << 0.10$] : $10^{-5} = 4x^2$ $= 0.0018\ M$ Molar solubility of $Ca(OH)_2 = 0.0018\ M$	1 point is earned for the correct stoichiometry and setup. 1 point is earned for the fi answer.

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

Represent water molecules as 



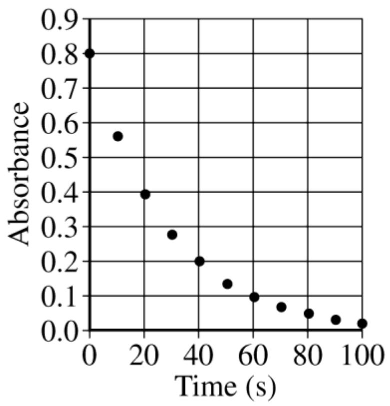
[The diagram should show the oxygen side of the water molecules oriented closer to the Ca^{2+} ion.]	1 point is earned for a correct diagram that shows at least three of the four water molecules oriented as described.

2015 SCORING GUIDELINES

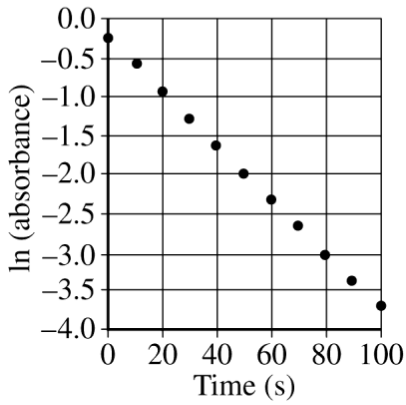
Question

$$\underset{blue}{Na_2C_{37}H_{34}N_2S_3O_9} + OCl^- \rightarrow \underset{colorless}{\text{products}}$$

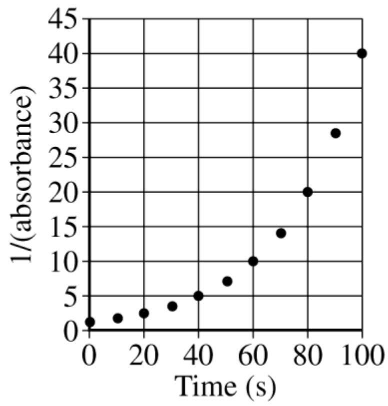
Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the 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 eaction 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.

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. 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. 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.	1 point is earned for choosing an appropriate pair of compounds (LiI/KI, LiI/LiF, or LiI/NaF 1 point is earned for an explanation that supports the hypothesis.

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. $+ H_2O \rightleftarrows HF + OH^-$	1 point is earned for choosing one of the correct compounds. 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. J + 10.7 kJ = 26 kJ	1 point is earned for calculating the amount 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.

$$Al_2O_3(s) \rightarrow 2\,Al(s) + \frac{3}{2}\,O_2(g) \qquad \Delta H^\circ = 1675\ \text{kJ/mol}_{rxn}$$

For extracting Al from ore: $1675\ \text{kJ/mol}_{rxn} \times \frac{1\ \text{mol of reaction}}{2\ \text{mol Al}} = 837.5\ \text{kJ per mol of Al}$ 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.