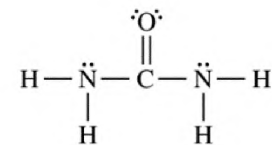


AP[®] Chemistry

Scoring Guidelines

2019 SCORING GUIDELINES

Question 1

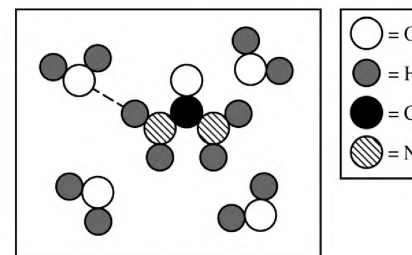


The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

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

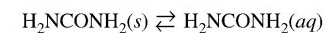
sp^2	1 point is earned for the correct answer.
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- (b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (---) to indicate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

2019 SCORING GUIDELINES

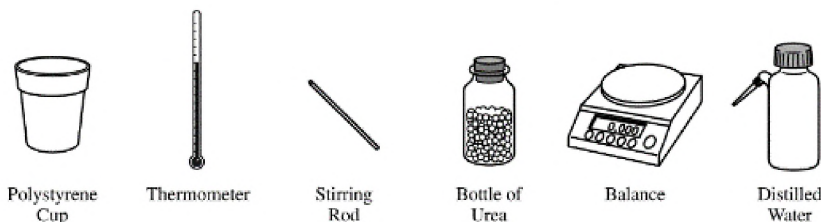
Question 1 (continued)

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

$5.39 \text{ g H}_2\text{NCONH}_2 \times \frac{1 \text{ mol}}{60.06 \text{ g}} = 0.0897 \text{ mol}$ $\frac{0.0897 \text{ mol}}{0.00500 \text{ L}} = 17.9 \text{ M}$	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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2019 SCORING GUIDELINES

Question 1 (continued)

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

- (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.

$\Delta S^\circ_{\text{soln}} = S^\circ(\text{H}_2\text{NCONH}_2(\text{aq})) - S^\circ(\text{H}_2\text{NCONH}_2(\text{s}))$ $70.1 \text{ J/(mol·K)} = S^\circ(\text{H}_2\text{NCONH}_2(\text{aq})) - 104.6 \text{ J/(mol·K)}$ $S^\circ(\text{H}_2\text{NCONH}_2(\text{aq})) = 174.7 \text{ J/(mol·K)}$	1 point is earned for the correct answer.
--	---

- (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.
--	--

- (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.
--	---

2019 SCORING GUIDELINES

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.



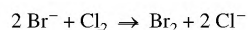
I₂ has the longest bond length because the radius of the I atom is greater than the radii of the other halogen atoms. Thus, the distance between the nuclei of atoms in I₂ is greater than it is in smaller halogens.

1 point is earned for circling I₂ and providing a valid explanation.

A chemistry teacher wants to prepare Br₂. The teacher has access to the following three reagents: NaBr(aq), Cl₂(g), and I₂(s).

Half-Reaction	E° at 25°C (V)
Br ₂ + 2 e ⁻ → 2 Br ⁻	1.07
Cl ₂ + 2 e ⁻ → 2 Cl ⁻	1.36
I ₂ + 2 e ⁻ → 2 I ⁻	0.53

- (b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br₂ when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of E° for the reaction.



1 point is earned for the correct balanced equation.

$$E^\circ = E^\circ(\text{reduced species}) - E^\circ(\text{oxidized species}) \\ = 1.36 \text{ V} - 1.07 \text{ V} = +0.29 \text{ V}.$$

Because E° for the reaction has a positive value, the reaction is thermodynamically favorable.

1 point is earned for the correct calculation of E°.

Br₂ and Cl₂ can react to form the compound BrCl.

- (c) The boiling point of Br₂ 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.

2019 SCORING GUIDELINES

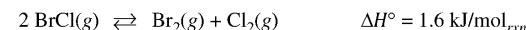
Question 2 (continued)

The only intermolecular attractions in Br₂(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 Br₂ compared to that of BrCl, the London forces in Br₂(l) are stronger than the combined intermolecular forces in BrCl(l). Thus, the boiling point of Br₂(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 Br₂ and Cl₂, as represented by the balanced chemical equation below.



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.

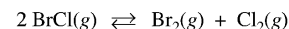
- (e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

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

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}.

2019 SCORING GUIDELINES

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)
Br – Br	193
Cl – Cl	243
Br – Cl	?

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

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

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

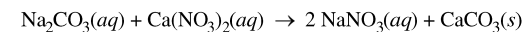
$$\text{Br–Cl bond energy} = 219 \text{ kJ/mol}$$

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

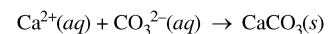
2019 SCORING GUIDELINES

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 $\text{Ca}(\text{NO}_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

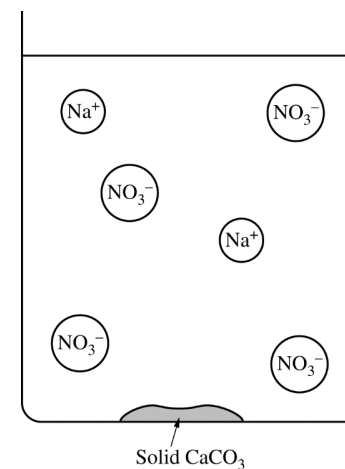


Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $\text{Ca}(\text{NO}_3)_2$ are mixed.



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.

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 $\text{Ca}(\text{NO}_3)_2$ 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.

$0.93 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g}} = 0.0093 \text{ mol CaCO}_3$	1 point is earned for the correct answer.
$0.0093 \text{ mol CaCO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CaCO}_3} = 0.0093 \text{ mol Na}_2\text{CO}_3$	

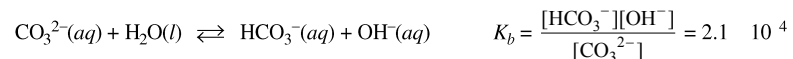
The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

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 ($\text{Na}^+(aq)$, $\text{CO}_3^{2-}(aq)$, and $\text{NO}_3^-(aq)$) 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, $\text{CO}_3^{2-}(aq)$ hydrolyzes to form $\text{HCO}_3^-(aq)$, as shown by the following equation.



2019 SCORING GUIDELINES

Question 3 (continued)

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

- (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.
--	---

- (ii) Explain how the student could use the measured value in part (f)(i) to calculate the initial concentration of $\text{CO}_3^{2-}(aq)$. (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^- .

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

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

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 $\text{HCO}_3^-(aq)$ greater than, less than, or equal to the concentration of $\text{CO}_3^{2-}(aq)$? 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.
---	--

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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2019 SCORING GUIDELINES

Question 4

dent is doing experiments with $\text{CO}_2(g)$. 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 $\text{CO}_2(g)$ in the container to 425 K.

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

average speed of the molecules increases as temperature increases.

1 point is earned for the correct answer.

Calculate the pressure of the $\text{CO}_2(g)$ in the container at 425 K.

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

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

1 point is earned for the correct answer.

In terms of kinetic molecular theory, briefly explain why the pressure of the $\text{CO}_2(g)$ 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 $\text{CO}_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

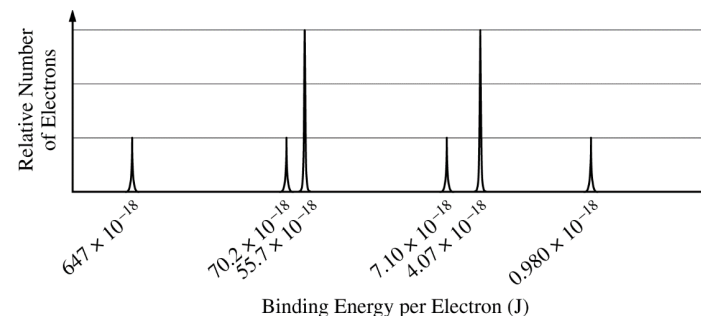
The attractive forces between CO_2 molecules result in a pressure that is lower than that predicted by the ideal gas law.

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 $[\text{Ar}] 4s^2$

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 = $0.980 \times 10^{-18} \text{ J}$

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

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

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

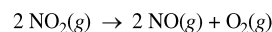
1 point is earned for the correct identification of the energy required to remove an electron from the valence shell (may be implicit).

1 point is earned for calculating the correct wavelength.

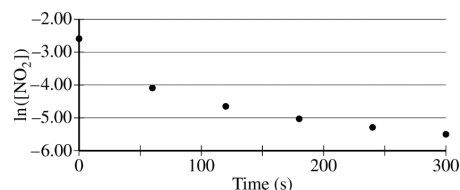
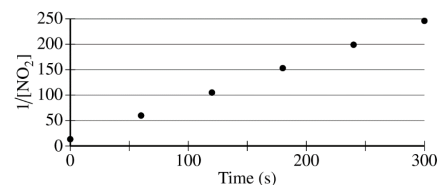
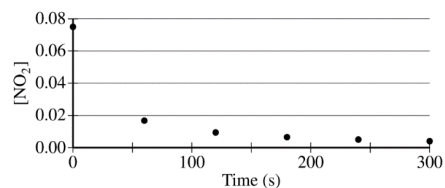
2019 SCORING GUIDELINES

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.

2019 SCORING GUIDELINES

Question 6 (continued)

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

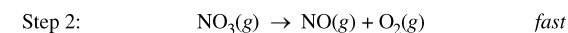
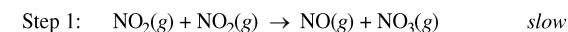
$$\text{rate} = k[\text{NO}_2]^2$$

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

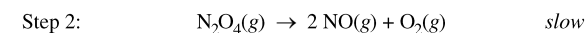


Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is $\text{rate} = k[\text{NO}_2][\text{NO}_2] = k[\text{NO}_2]^2$, which is consistent with the second-order rate law in part (b).

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

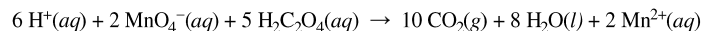


Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is $\text{rate} = k[\text{N}_2\text{O}_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$ 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.

2019 SCORING GUIDELINES

Question 7



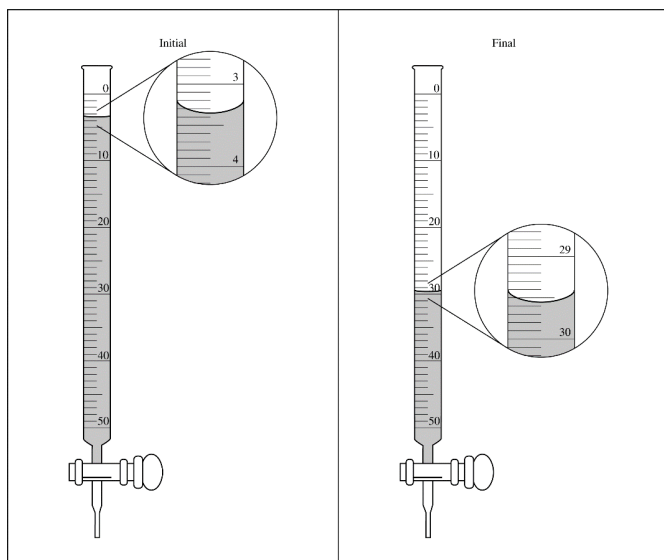
A student dissolved a 0.139 g sample of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, in water in an Erlenmeyer flask. Then the student titrated the $\text{H}_2\text{C}_2\text{O}_4$ solution in the flask with a solution of KMnO_4 , which has a dark purple color. The balanced chemical equation for the 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 $\text{KMnO}_4(aq)$ to the $\text{H}_2\text{C}_2\text{O}_4(aq)$ 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 $\text{KMnO}_4(aq)$ that was added during the titration.



$$29.55 \text{ mL} - 3.35 \text{ mL} = 26.20 \text{ mL}$$

1 point is earned for the correct answer.

2019 SCORING GUIDELINES

Question 7 (continued)

Given that the concentration of $\text{KMnO}_4(aq)$ was 0.0235 M, calculate the number of moles of MnO_4^- 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

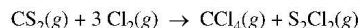
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AP Chemistry

Scoring Guidelines

2017 SCORING GUIDELINES

Question 1



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

(i) How many moles of $\text{Cl}_2(\text{g})$ are in the container?

$n = \frac{PV}{RT} = \frac{0.40 \text{ atm} \times 25.0 \text{ L}}{0.08206 (\text{L} \cdot \text{atm})/(\text{mol} \cdot \text{K}) \times 393 \text{ K}} = 0.31 \text{ mol } \text{Cl}_2(\text{g})$	1 point is earned for the correct answer with supporting work.
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(ii) How many grams of carbon disulfide, $\text{CS}_2(\text{g})$, are needed to react completely with the $\text{Cl}_2(\text{g})$?

$0.31 \text{ mol } \text{Cl}_2 \times \frac{1 \text{ mol } \text{CS}_2}{3 \text{ mol } \text{Cl}_2} \times \frac{76.13 \text{ g } \text{CS}_2}{1 \text{ mol } \text{CS}_2} = 7.9 \text{ g } \text{CS}_2$	1 point is earned for using the correct mole ratio (may be implicit). 1 point is earned for the mass of CS_2 .
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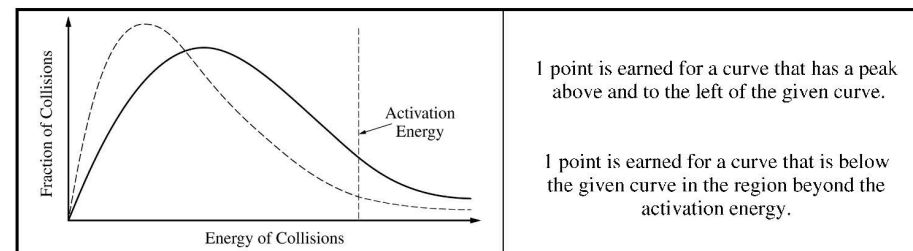
(b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C , the reaction occurs at an observable rate.

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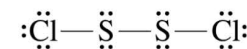
(ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C .

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.

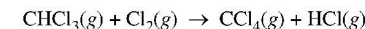
1 point is earned for a correctly drawn diagram.

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



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

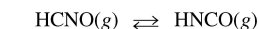
In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of -1 . In the diagram on the right, the C atom has a formal charge of -1 and the O atom has a formal charge of zero.

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*

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

- (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
- $\text{HCNO}(g)$
- to form
- $\text{HNCO}(g)$
- .

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 $\Delta G^\circ \approx -246 \text{ kJ/mol}_{rxn}$, 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.)

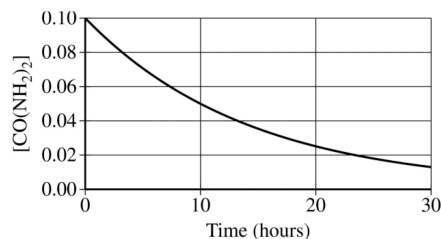
1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K .

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

- (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.

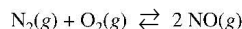
- (f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $\text{OH}^-(aq)$.

Perform the experiment at a different concentration of $\text{OH}^-(aq)$ and measure how the concentration of $\text{CO}(\text{NH}_2)_2$ 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, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

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

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})}$$

1 point is earned for a correct K_p expression.

- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

	$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$		
Initial	6.01	1.61	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$6.01-x$	$1.61-x$	0.122

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

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

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

1 point is earned for the correct calculation of K_p .

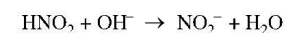
Nitrogen monoxide, $\text{NO}(\text{g})$, can undergo further reactions to produce acids, such as HNO_2 , a weak acid with a K_a of 4.0×10^{-4} and a $\text{p}K_a$ of 3.40.

- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.

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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 $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ 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 $\text{NaOH}(\text{aq})$.

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

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

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).

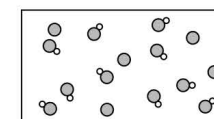
- (d) A second student makes a buffer by dissolving 0.100 mol of $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student 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 $\text{HNO}_2(\text{aq})$ 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

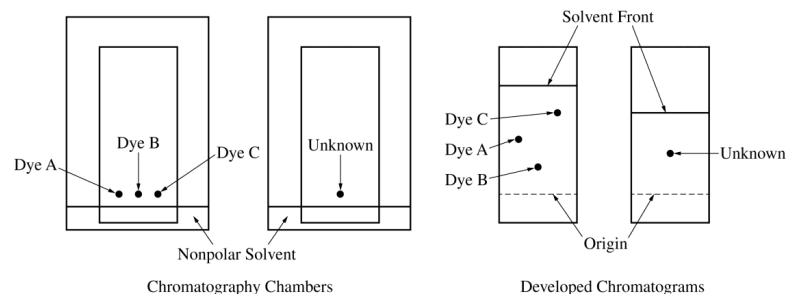
$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \Rightarrow \text{pH} = 3.40 + \log \frac{5}{10} \Rightarrow \text{pH} = 3.10$$

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.

Nonpolar dyes are more strongly attracted to the nonpolar solvent.

AND/OR

Nonpolar dyes are least strongly retained by the polar paper.

1 point is earned for the correct choice **and** reference to the chromatogram.

1 point is earned for a correct description of dye-solvent **and/or** dye-paper interactions.

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

Dye A is present in the unknown sample.

The unknown sample moves to a position that is midway between the origin and the solvent front, and so does dye A.

OR

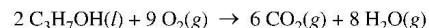
Dye A has a retention factor (R_f) that is close to 0.50 on the chromatogram with the three dyes, and the unknown also has a retention factor close to 0.50.

1 point is earned for the correct choice.

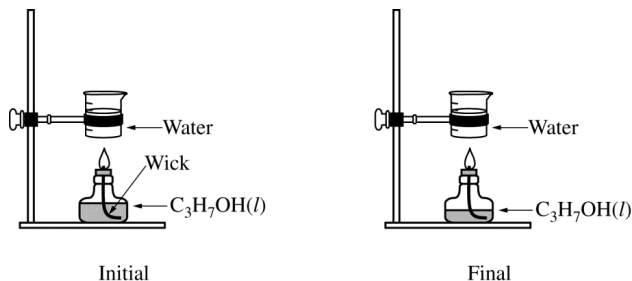
1 point is earned for a valid justification.

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Question 5



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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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.

- (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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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 $100. \text{ mL}$ 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.

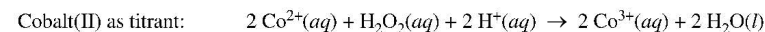
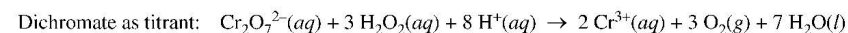
1 point is earned for the correct comparison of cation sizes.

1 point is earned for indicating that smaller interionic distances lead to a greater lattice energy.

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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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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° .