

2017

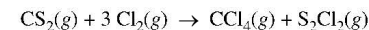
AP[®] CollegeBoard

AP Chemistry

Scoring Guidelines

2017 SCORING GUIDELINES

Question 1



Carbon tetrachloride, $\text{CCl}_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.

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

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

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

$0.31 \text{ mol } \text{Cl}_2 \times \frac{1 \text{ mol } \text{CS}_2}{3 \text{ mol } \text{Cl}_2} \times \frac{76.13 \text{ g } \text{CS}_2}{1 \text{ mol } \text{CS}_2} = 7.9 \text{ g } \text{CS}_2$	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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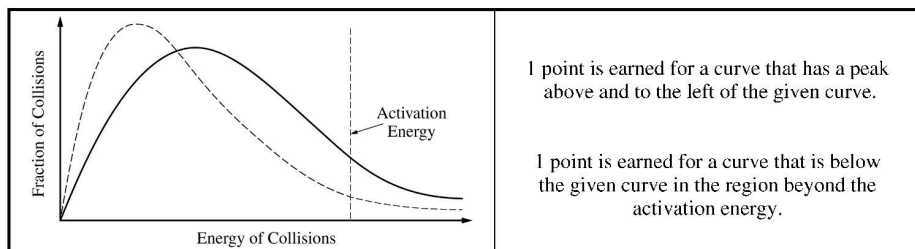
(b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C , the reaction occurs at an observable rate.

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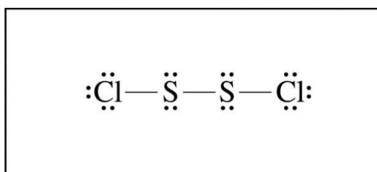
(ii) The graph below shows a distribution for the collision energies of reactant molecules at 120°C . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C .

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.

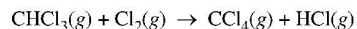
1 point is earned for a correctly drawn diagram.

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



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

Question 1 (continued)

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

Dipole-dipole forces, London dispersion forces

1 point is earned for both types of forces.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $\text{CCl}_4(l)$ and $\text{HCl}(l)$? Justify your answer in terms of the information above.

The intermolecular forces among CCl_4 molecules must be **stronger** than those among HCl molecules because the CCl_4 condenses at a higher temperature than HCl .

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

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Question 2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.



- (a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

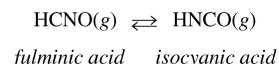
In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of -1 . In the diagram on the right, the C atom has a formal charge of -1 and the O atom has a formal charge of zero.

The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon.

1 point is earned for a correct assignment of formal charges in the two diagrams.

1 point is earned for a correct explanation.

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



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

- (b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of HCNO(g) to form HNCO(g).

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

Compound	HCNO	HNCO
Bond Enthalpies (kJ/mol)	413 + 891 + 201	391 + 615 + 745
Total Bond Enthalpy (kJ/mol)	1505	1751

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

1 point is earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken.

1 point is earned for the correct determination of ΔH° .

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Question 2 (continued)

- (c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

The change from fulminic acid to isocyanic acid is a rearrangement of atoms with no change in phase or number of molecules.

1 point is earned for a correct explanation.

- (d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

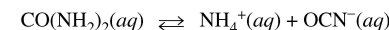
Isocyanic acid (HNCO) will be present in higher concentration.
 ΔG° is essentially equal to ΔH° because ΔS° is essentially zero, so $\Delta G^\circ \approx -246 \text{ kJ/mol}_{\text{rxn}}$, indicating the forward reaction is thermodynamically favorable.

Since ΔG° is negative, $K > 1$ ($\Delta G^\circ = -RT \ln K$), resulting in a higher concentration of product than reactant at equilibrium.

1 point is earned for the correct choice **with** a valid justification.
(Calculation of ΔG° is a sufficient justification.)

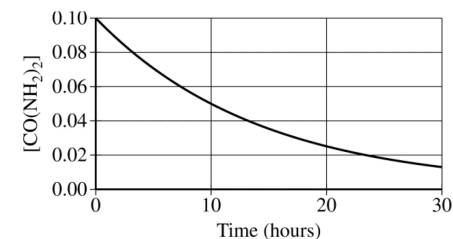
1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K .

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



A student studying the decomposition reaction runs the reaction at 90°C . The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



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Question 2 (continued)

(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

From inspecting the data table or the graph, it is evident that the decomposition reaction has a constant half-life, which indicates that the reaction is a first-order reaction.

1 point is earned for a correct explanation.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k . Include units with your answer.

Since the reaction is first order,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10. \text{ h}} = 0.069 \text{ h}^{-1}$$

OR

$$k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.1000) - \ln(0.0500)}{10. \text{ h}} = 0.069 \text{ h}^{-1}$$

1 point is earned for the correct value of k with correct units.

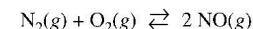
(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

Perform the experiment at a different concentration of $OH^-(aq)$ and measure how the concentration of $CO(NH_2)_2$ changes over time.
(Other variables, such as temperature, should be held constant.)

1 point is earned for the description of a valid experiment.

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Question 3



At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

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

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

1 point is earned for a correct K_p expression.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p .

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

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

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

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

1 point is earned for the correct calculation of K_p .

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

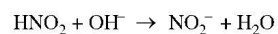
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

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Question 3 (continued)

NaOH will neutralize some of the HNO_2 to produce NO_2^- . The resulting solution contains a mixture of a weak acid and its conjugate base, which is a buffer solution.



1 point is earned for the recognition that the solution produced is a mixture of a weak acid and its conjugate base.

1 point is earned for the correct net ionic equation.

- (ii) Determine the volume, in mL, of 0.100 M NaOH(aq) the student should add to 100. mL of 0.100 M HNO_2 (aq) to make a buffer solution with a pH of 3.40. Justify your answer.

The student should add 50.0 mL of 0.100 M NaOH(aq).

When half of the HNO_2 is converted to the conjugate base,

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

OR

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

1 point is earned for the correct volume.

1 point is earned for clearly indicating a 1 to 1 ratio of HNO_2 and NO_2^- (calculation not required).

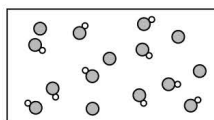
- (d) A second student makes a buffer by dissolving 0.100 mol of NaNO_2 (s) in 100. mL of 1.00 M HNO_2 (aq). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.

The buffer made by the second student is more resistant to changes in pH because it contains a higher concentration of HNO_2 and NO_2^- to react with added H^+ or OH^- ions.

1 point is earned for the correct choice and a valid justification.

- (e) A new buffer is made using HNO_2 (aq) as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.

● HNO_2 molecule ● NO_2^- ion



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Question 3 (continued)

The pH of the solution is less than 3.40.

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

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

OR

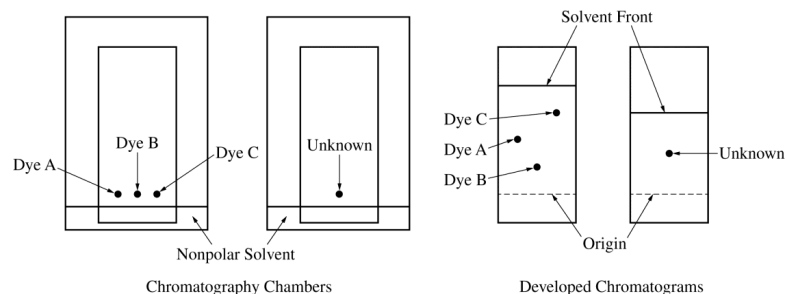
$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \Rightarrow \text{pH} = 3.40 + \log \frac{5}{10} \Rightarrow \text{pH} = 3.10$$

1 point is earned for the correct choice.

1 point is earned for a valid justification.

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Question 4



A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.

- (a) Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

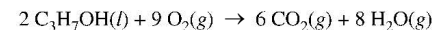
Dye C is the least polar because it moved the farthest.	1 point is earned for the correct choice and reference to the chromatogram.
Nonpolar dyes are more strongly attracted to the nonpolar solvent. AND/OR Nonpolar dyes are least strongly retained by the polar paper.	1 point is earned for a correct description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

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

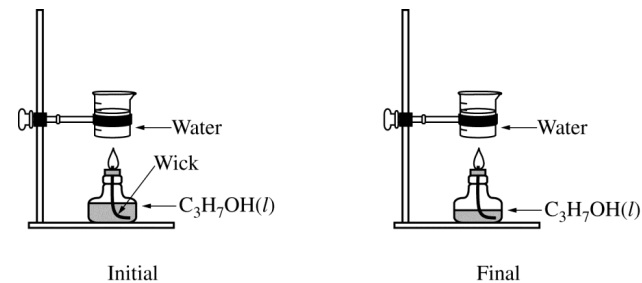
Dye A is present in the unknown sample.	1 point is earned for the correct choice.
The unknown sample moves to a position that is midway between the origin and the solvent front, and so does dye A. OR Dye A has a retention factor (R_f) that is close to 0.50 on the chromatogram with the three dyes, and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

2017 SCORING GUIDELINES

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.
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- (c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $\text{C}_3\text{H}_7\text{OH}(l)$ that is contaminated with water, which is miscible with $\text{C}_3\text{H}_7\text{OH}(l)$. The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

The final temperature measured by the second student would be less than that measured by the first student because: the actual mass of $\text{C}_3\text{H}_7\text{OH}(l)$ combusted will be less than 0.55 g OR combustion of the contaminated sample will also require vaporization of the water in the sample.	1 point is earned for the correct choice with a valid explanation.
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2017 SCORING GUIDELINES

Question 6

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

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

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

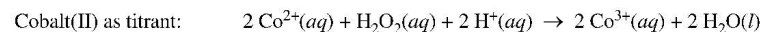
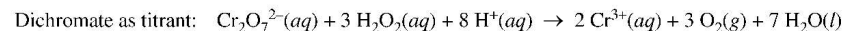
Reaction	Lattice Energy (kJ/mol)
$\text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(g) + 2 \text{ OH}^-(g)$	2900
$\text{Sr}(\text{OH})_2(s) \rightarrow \text{Sr}^{2+}(g) + 2 \text{ OH}^-(g)$	2300

The Sr^{2+} ion is larger than the Mg^{2+} ion because it has additional occupied energy levels (or shells). Coulomb's law states that the force of attraction between cation and anion is inversely proportional to the square of the distance between them. Since the distance between Mg^{2+} and OH^- is shorter than the distance between Sr^{2+} and OH^-, the attractive forces in $\text{Mg}(\text{OH})_2$ are stronger and, therefore, its lattice energy is greater.	1 point is earned for the correct comparison of cation sizes. 1 point is earned for indicating that smaller interionic distances lead to a greater lattice energy.
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2017 SCORING GUIDELINES

Question 7

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



The half-reactions and the E° values for the systems related to the titrations above are given in the following table.

Half-Reaction	E° (V) at 298 K
$\text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq)$	1.84
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.77
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70

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

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

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

$E^\circ = -1.84 + 1.77 = -0.07 \text{ V}$	1 point is earned for correctly combining E° values.
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2017 SCORING GUIDELINES

Question 7 (continued)

(b) Based on the calculated values of E° , the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

(i) Which titrant should the student choose? Explain your reasoning.

The student should use the dichromate ion for the titration because, for the reaction, the value of E° is positive, which means that the reaction is thermodynamically favorable.

OR

$\Delta G^\circ = -nFE^\circ$ and n , F , and E° are all positive numbers, therefore $\Delta G^\circ < 0$, which means that the reaction is thermodynamically favorable.

1 point is earned for choosing the correct titrant **and** for understanding that a positive E° or a negative ΔG° is required.

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

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

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