

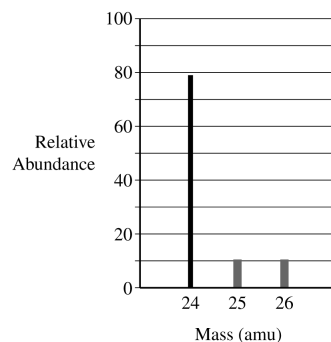
## Question 1: Long Answer

10 points

A (i) For the correct plotted lines:

Point 01

The abundance for the two lines should be between 10 and 11.



(ii) For the correct answer:

Point 02

Magnesium-26 has one more neutron than magnesium-25 does.

B (i) For a correct explanation:

Point 03

The charge on the sodium ion is less than the charge on the magnesium ion. A smaller charge results in a weaker Coulombic attraction between  $\text{Na}^+$  and water.

(ii) For a correct explanation:

Point 04

The  $\text{Na}^+$  ion is larger than the  $\text{Mg}^{2+}$  ion, so the distance between the  $\text{Na}^+$  and the oxygen on the water molecule will be greater. As distance increases, Coulombic attraction decreases.

C For the correct calculated value:

Point 05

$$\text{pOH} = -\log(2.80 \times 10^{-4}) = 3.553$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.553 = 10.447$$

D For the correct calculated value:

Point 06

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{(1.85 \times 10^{-3} M)(0.03500 \text{ L})}{(0.03500 \text{ L} + 0.05000 \text{ L})} = 7.62 \times 10^{-4} M$$

E (i) For the correct expression:

Point 07

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

(ii) For the correct calculated value, consistent with part D and part E (i):

Point 08

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (7.62 \times 10^{-4})(1.65 \times 10^{-4})^2 = 2.07 \times 10^{-11}$$

(iii) For the correct prediction and justification, consistent with part E (ii).

Point 09

Examples of acceptable responses may include the following:

- $Q > K_{sp}$ , so a precipitate will form.
- The concentration of the ions in solution (represented by  $Q$ ) is greater than that of a saturated solution, so a precipitate will form.

F For the correct answer and justification:

Point 10

Decrease. The  $\text{H}^+$  from  $\text{HNO}_3(aq)$  will react with  $\text{OH}^-$ , decreasing  $[\text{OH}^-]$  and causing  $Q < K_{sp}$ . As a result, more  $\text{Mg}(\text{OH})_2(s)$  will dissolve until equilibrium is reestablished, resulting in less  $\text{Mg}(\text{OH})_2(s)$ .

## Question 3: Long Answer

10 points

A For the correct diagram: **Point 01**

B (i) For a correct explanation: **Point 02**

*Because gas particles are more dispersed (have more microstates) than solids, the entropy decreases as the reactants (which include a gas) convert to the solid product.*

(ii) For the correct answer and a valid justification: **Point 03**

*Yes. Given that  $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$ , the reaction must have  $\Delta G_{rxn}^\circ < 0$  to be favorable. Because the reaction is exothermic,  $\Delta H_{rxn}^\circ < 0$  and enthalpy contributes to favorability.  $\Delta S_{rxn}^\circ < 0$ , so entropy does not contribute to favorability.*

C (i) For the correct calculated value reported with the correct number of significant figures: **Point 04**

$$q = mc\Delta T = (100.1 \text{ g})(4.18 \text{ J/(g}\cdot^\circ\text{C)})(22.38^\circ\text{C} - 22.00^\circ\text{C})$$

$$q = 160 \text{ J} = 0.16 \text{ kJ}$$

(ii) For the correct calculated value, consistent with part C (i): **Point 05**

$$q_{rxn} = -q_{surr} = -0.16 \text{ kJ}$$

$$\Delta H_{rxn}^\circ = \frac{-0.16 \text{ kJ}}{0.100 \text{ g P}_4\text{O}_{10}} \times \frac{283.9 \text{ g P}_4\text{O}_{10}}{1 \text{ mol P}_4\text{O}_{10}} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{1 \text{ mol}_{rxn}} = -450 \text{ kJ/mol}_{rxn}$$

For the correct sign: **Point 06**

$$-450 \text{ kJ/mol}_{rxn}$$

D For the correct answer and a valid justification: **Point 07**

*Less than. If less  $\text{P}_4\text{O}_{10}$  is present, less thermal energy will be transferred to the water during the reaction, causing the temperature increase to be less than it was with 0.100 g of  $\text{P}_4\text{O}_{10}$ .*

E For the correct calculated value: **Point 08**

*Using Hess's law:*

$$\Delta H_{f, \text{PCl}_5(\text{g})}^\circ = \frac{1}{4}\Delta H_1^\circ + \Delta H_2^\circ$$

$$\Delta H_{f, \text{PCl}_5(\text{g})}^\circ = \frac{1}{4}(-1148) + (-88) = -375 \text{ kJ/mol}$$

F (i) For the correct calculated value: **Point 09**

$$K_p = \frac{P_{\text{PCl}_5}}{(P_{\text{PCl}_3})(P_{\text{Cl}_2})} = \frac{4.00}{(2.00)(6.00)} = \frac{1}{3} = 0.333$$

(ii) For the correct answer and a valid justification: **Point 10**

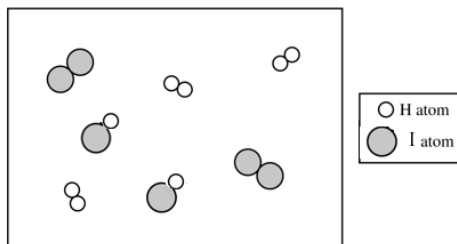
*Decrease. The negative value of  $\Delta H_2^\circ$  indicates that the reaction is exothermic. Because exothermic reactions favor reactant formation at higher temperature, the value of  $K_p$  decreases.*

## Question 5: Short Answer 4 points

- (a) For the correct expression: 1 point

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

- (b) (i) For the correct drawing consistent with part (a): 1 point



- (ii) For a valid hypothesis: 1 point

Accept one of the following:

- Decreased the temperature.
- Added more  $\text{H}_2$  and/or  $\text{I}_2$  to the reaction vessel.

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

Accept one of the following:

- Remain unchanged. The number of moles in the numerator and denominator of  $Q$  (or  $K$ ) are equal; changing the volume of the container would not alter the value of  $Q$ , which is still equal to  $K$ , so the number of moles of HI will remain the same.
- Remain unchanged. The increase in volume will decrease the concentration of reactants and products by an equal proportion. Because there are equal moles of gaseous reactants and products in the balanced chemical equation, there is no shift in the equilibrium position, and the number of moles of HI will remain the same.

Total for part (b) 3 points

Total for question 5 4 points

## Question 2: Long Answer 10 points

- (a) For the correct calculated value reported with the correct number of significant figures: 1 point

$$1.25 \text{ mol AlCl}_3 \times \frac{3 \text{ mol Cl}}{1 \text{ mol AlCl}_3} \times \frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}} = 133 \text{ g Cl}$$

- (b) For the correct algebraic manipulation of either
- $\Delta H_2^\circ$
- or
- $\Delta H_4^\circ$
- (may be implicit): 1 point

Accept one of the following:

- Reversing reaction 2:



- Multiplying reaction 4 by  $\frac{3}{2}$ :



For the correct calculated value: 1 point

$$\Delta H_1^\circ = -\Delta H_2^\circ + \Delta H_3^\circ + 1.5(\Delta H_4^\circ) = -(-583) + 326 + 1.5(243) = 1274 \text{ kJ/mol}_{\text{rxn}}$$

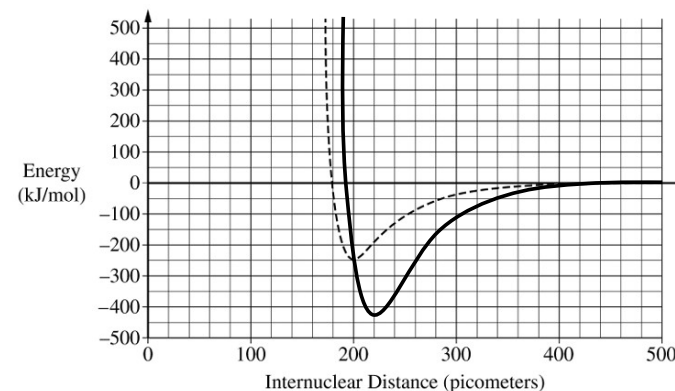
Total for part (b) 2 points

- (c) (i) For the correct answer: 1 point

200 picometers ( $\pm 10 \text{ pm}$ )

- (ii) For a curve with a minimum at an internuclear distance of
- $220 \pm 10 \text{ pm}$
- : 1 point

See sample curve below

For a curve with a minimum energy value of  $-425 \pm 20 \text{ kJ/mol}$  that approaches zero as the internuclear distance approaches 500 pm: 1 point

Total for part (c) 3 points

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

Diagram 2. Al has four electron domains in Diagram 2, which would be trigonal pyramidal, not trigonal planar.

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

Diagram 1. All atoms in diagram 1 have a formal charge of zero, whereas atoms in diagrams 2 and 3 have nonzero formal charges.

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

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

$$K_p = \frac{P_{\text{Al}_2\text{Cl}_6}}{(P_{\text{AlCl}_3})^2}$$

(f) For the correct calculated value, consistent with part (e): **1 point**

$$K_p = \frac{\chi_{\text{Al}_2\text{Cl}_6}(P_{\text{total}})}{(\chi_{\text{AlCl}_3}(P_{\text{total}}))^2} = \frac{\frac{3}{10}(22.1)}{\left(\frac{7}{10}(22.1)\right)^2} = 0.0277$$

**Total for question 2 10 points**

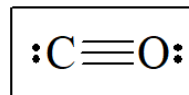
## Question 2: Long Answer

**10 points**

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

The H atoms are reduced because they change from an oxidation number of +1 to 0.

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



(c) (i) For the correct stoichiometry (may be implicit): **1 point**

$$\Delta S^\circ_{\text{rxn}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{reactants}}$$

$$\Delta S^\circ_{\text{rxn}} = (\Delta S^\circ_{\text{CO(g)}} + 2(\Delta S^\circ_{\text{H}_2\text{(g)}})) - (\Delta S^\circ_{\text{CH}_3\text{OH(g)}})$$

For the correct calculated value: **1 point**

$$\Delta S^\circ_{\text{rxn}} = 198 + 2(131) - 240. = 220. \frac{\text{J}}{\text{K}\cdot\text{mol}_{\text{rxn}}}$$

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

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

$$\Delta G^\circ = 90.0 \frac{\text{kJ}}{\text{mol}_{\text{rxn}}} - (375 \text{ K})(0.220 \frac{\text{kJ}}{\text{K}\cdot\text{mol}_{\text{rxn}}}) = +7.5 \text{ kJ/mol}_{\text{rxn}}$$

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

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

$$P_{\text{CO}} = \frac{3}{10} (12.0 \text{ atm}) = 3.6 \text{ atm}$$

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

$$K_p = \frac{(P_{\text{CO}})(P_{\text{H}_2})^2}{(P_{\text{CH}_3\text{OH}})}$$

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

$$K_p = \frac{(P_{\text{CO}})(P_{\text{H}_2})^2}{(P_{\text{CH}_3\text{OH}})} = \frac{(4.2)(8.4)^2}{(2.7)} = 110$$

(g) For a correct comparison of  $Q$  and  $K$ :

1 point

Accept one of the following:

- The change in volume causes the partial pressure of each species to decrease by a factor of two. Because there are more moles of gaseous products than reactants, the decrease of the numerator in  $Q$  will be larger than that in the denominator, making  $Q_p < K_p$ .

$$Q_p = \frac{\left(\frac{P_{\text{CO}}}{2}\right)\left(\frac{P_{\text{H}_2}}{2}\right)^2}{\left(\frac{P_{\text{CH}_3\text{OH}}}{2}\right)} = \frac{K_p}{4} \approx 27 < K_p$$

For the correct answer and a valid justification:

1 point

Decrease. Given that  $Q_p < K_p$ , the partial pressures (moles) of the products will increase as equilibrium re-establishes, decreasing the number of moles of  $\text{CH}_3\text{OH}$ .

Total for part (g) 2 points

Total for question 2 10 points

## Question 1: Long Answer

10 points

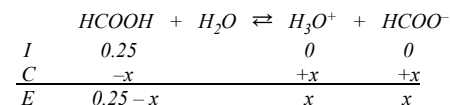
(a) For the correct expression:

1 point

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

(b) For the correct calculated concentration of  $\text{H}_3\text{O}^+$ :

1 point



$$\text{Let } [\text{H}_3\text{O}^+] = x, \text{ then } 1.8 \times 10^{-4} = \frac{x^2}{(0.25 - x)}$$

$$\text{Assume } x \ll 0.25, \text{ then } 1.8 \times 10^{-4} = \frac{x^2}{0.25} \Rightarrow x = 0.0067 \text{ M}$$

For the correct calculated value of pH:

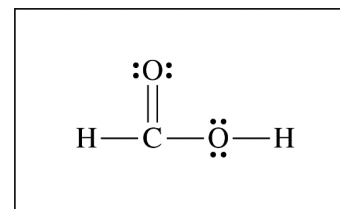
1 point

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0067) = 2.17$$

Total for part (b) 2 points

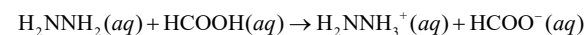
(c) For the correct diagram:

1 point



(d) (i) For the correct balanced equation (state symbols not required):

1 point



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

1 point

Acidic. The  $K_a$  of  $\text{H}_2\text{NNH}_3^+$  is greater than the  $K_b$  of  $\text{HCOO}^-$ , so the production of  $\text{H}_3\text{O}^+(aq)$  occurs to a greater extent than the production of  $\text{OH}^-(aq)$ .

Total for part (d) 2 points

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

1 point

Accept one of the following:

- Yes. The oxidation number of hydrogen changes from +1 in  $\text{HCOOH}$  to zero in  $\text{H}_2$ .
- Yes. The oxidation number of carbon changes from +2 in  $\text{HCOOH}$  to +4 in  $\text{CO}_2$ .

(f) For the correct calculated value of the pressure of CO<sub>2</sub> (may be implicit): **1 point**

$$24 \text{ atm total} \times 1 \text{ atm CO}_2 / 2 \text{ atm of product} = 12 \text{ atm CO}_2$$

For the correct calculated number of moles of CO<sub>2</sub>: **1 point**

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(12 \text{ atm})(4.3 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.1 \text{ mol CO}_2$$

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

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

*It would remain the same. In a catalyzed reaction the net amount of catalyst is constant.*

**Total for question 1 10 points**

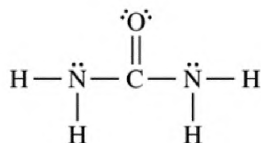
2019

# AP<sup>®</sup> Chemistry

## Scoring Guidelines

## 2019 SCORING GUIDELINES

## Question 1

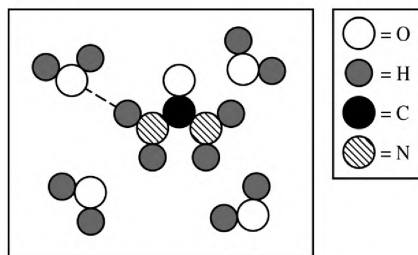


The compound urea,  $\text{H}_2\text{NCONH}_2$ , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

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

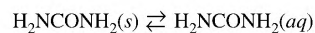
|        |                                           |
|--------|-------------------------------------------|
| $sp^2$ | 1 point is earned for the correct answer. |
|--------|-------------------------------------------|

- (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.



The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of  $\text{H}_2\text{NCONH}_2$  (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.

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

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

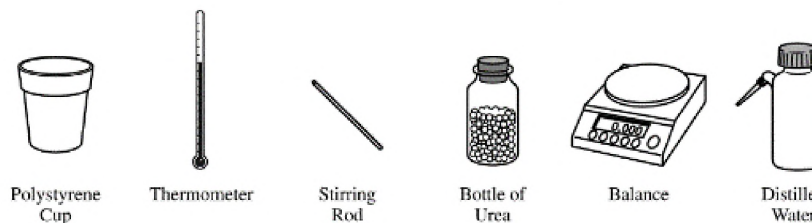
1 point is earned for the correct number of moles of urea (may be implicit).

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.

## 2019 SCORING GUIDELINES

## Question 1 (continued)

|                                       | $S^\circ$ (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,  $S^\circ$ , 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  $\Delta S^\circ$  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 $\Delta G^\circ$ , with $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . Since $\Delta S^\circ$ is positive, the $T\Delta S^\circ$ term makes the value of $\Delta G^\circ$ 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.

$\text{Br}_2$                        $\text{Cl}_2$                        $\text{F}_2$                        $\text{I}_2$

|                                                                                                                                                                                                                                           |                                                                                |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| $\text{I}_2$ 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 $\text{I}_2$ is greater than it is in smaller halogens. | 1 point is earned for circling $\text{I}_2$ and providing a valid explanation. |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|

A chemistry teacher wants to prepare  $\text{Br}_2$ . The teacher has access to the following three reagents:  $\text{NaBr}(\text{aq})$ ,  $\text{Cl}_2(\text{g})$ , and  $\text{I}_2(\text{s})$ .

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

- (b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce  $\text{Br}_2$  when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of  $E^\circ$  for the reaction.

|                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                           |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| $2 \text{Br}^- + \text{Cl}_2 \rightarrow \text{Br}_2 + 2 \text{Cl}^-$ $E^\circ = E^\circ(\text{reduced species}) - E^\circ(\text{oxidized species})$ $= 1.36 \text{ V} - 1.07 \text{ V} = +0.29 \text{ V}$ <p>Because <math>E^\circ</math> for the reaction has a positive value, the reaction is thermodynamically favorable.</p> | <p>1 point is earned for the correct balanced equation.</p> <p>1 point is earned for the correct calculation of <math>E^\circ</math>.</p> |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|

$\text{Br}_2$  and  $\text{Cl}_2$  can react to form the compound  $\text{BrCl}$ .

- (c) The boiling point of  $\text{Br}_2$  is 332 K, whereas the boiling point of  $\text{BrCl}$  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

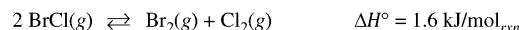
## Question 2 (continued)

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

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

1 point is earned for a valid explanation.

The compound  $\text{BrCl}$  can decompose into  $\text{Br}_2$  and  $\text{Cl}_2$ , as represented by the balanced chemical equation below.



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

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

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

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

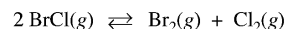
(e) Write the expression for the equilibrium constant,  $K_{eq}$ , for the decomposition of  $\text{BrCl}$ .

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

1 point is earned for a correct equilibrium expression.

After the system has reached equilibrium, 42 percent of the original  $\text{BrCl}$  sample has decomposed.

(f) Determine the value of  $K_{eq}$  for the decomposition reaction of  $\text{BrCl}$  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  $\text{Br-Cl}$  bond, in  $\text{kJ/mol}$ , using  $\Delta H^\circ$  for the reaction (1.6  $\text{kJ/mol}$  information in the following table.

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

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

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

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

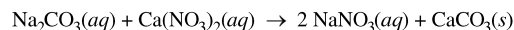
$$\text{Cl bond energy} = 219 \text{ kJ/mol}$$

1 point is earned for a correct calculation of the  $\text{Br-Cl}$  bond energy.

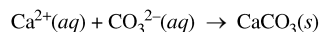
## 2019 SCORING GUIDELINES

## Question 3

A student is given 50.0 mL of a solution of  $\text{Na}_2\text{CO}_3$  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.

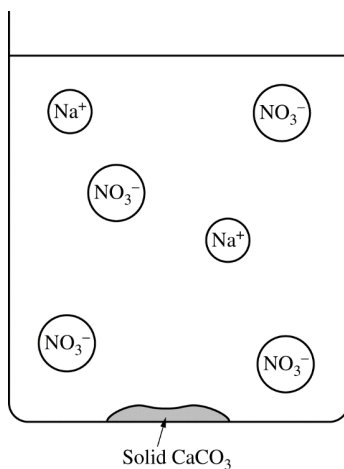


Write the net ionic equation for the reaction that occurs when the solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  are mixed.



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  $\text{Ca}^{2+}$  ion.

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

## 2019 SCORING GUIDELINES

## Question 3 (continued)

The student filters and dries the precipitate of  $\text{CaCO}_3$  (molar mass 100.1 g/mol) and records the data in the table below.

|                                                  |          |
|--------------------------------------------------|----------|
| Volume of $\text{Na}_2\text{CO}_3$ solution      | 50.0 mL  |
| Volume of 1.0 M $\text{Ca}(\text{NO}_3)_2$ added | 100.0 mL |
| Mass of $\text{CaCO}_3$ precipitate collected    | 0.93 g   |

Determine the number of moles of  $\text{Na}_2\text{CO}_3$  in the original 50.0 mL of solution.

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

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

1 point is earned for the correct answer.

The student realizes that the precipitate was not completely dried and claims that as a result, the calculated  $\text{Na}_2\text{CO}_3$  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  $\text{CaCO}_3$ . As a result, the calculated number of moles of  $\text{CaCO}_3$  and moles of  $\text{Na}_2\text{CO}_3$  will be greater than the actual moles present. Therefore the calculated concentration of  $\text{Na}_2\text{CO}_3(aq)$  will be too high.

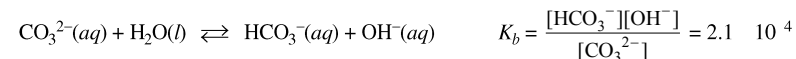
1 point is earned for the correct answer with valid justification.

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

The liquid conducts electricity because ions ( $\text{Na}^+(aq)$ ,  $\text{NO}_3^-(aq)$ , and  $\text{NaNO}_3(aq)$ ) 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  $\text{Na}_2\text{CO}_3$  solution using a second method. When it is dissolved in water,  $\text{CO}_3^{2-}(aq)$  hydrolyzes to form  $\text{HCO}_3^-(aq)$ , as shown by the following equation.



## 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  $\text{CO}_3^{2-}(\text{aq})$ .

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

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

- (ii) Explain how the student could use the measured value in part (f)(i) to calculate the initial concentration of  $\text{CO}_3^{2-}(\text{aq})$ . (Do not do any numerical calculations.)

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

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

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

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

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

1 point is earned for a valid method of determining the initial concentration of  $\text{CO}_3^{2-}$ .

In the original  $\text{Na}_2\text{CO}_3$  solution at equilibrium, is the concentration of  $\text{HCO}_3^-(\text{aq})$  greater than, less than, or equal to the concentration of  $\text{CO}_3^{2-}(\text{aq})$ ? Justify your answer.

|                                                                                                   |                                                                      |
|---------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
| Less than. The small value of $K_b$ , $2.1 \times 10^{-4}$ , 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  $\text{Na}_2\text{CO}_3$  solution suitable for making a buffer with a pH of 6? Explain why or why not.

|                                                                                                                                                                                                                                                                                                              |                                                                    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| The $\text{Na}_2\text{CO}_3$ solution is not suitable. The $\text{p}K_a$ of $\text{HCO}_3^-$ 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. |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|

## 2019 SCORING GUIDELINES

## Question 4

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

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

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

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

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

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

1 point is earned for the correct answer.

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

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

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

1 point is earned for a correct explanation.

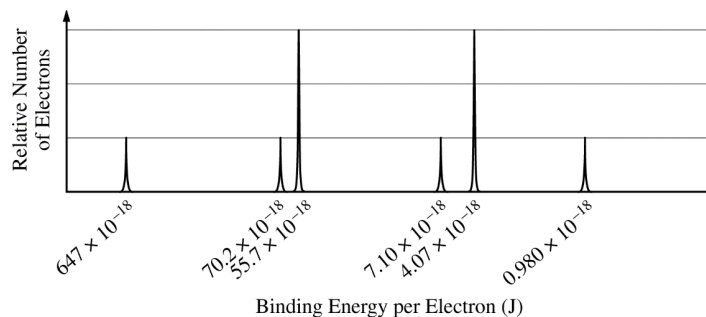
The student measures the actual pressure of the  $\text{CO}_2(\text{g})$  in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

|                                                                                                                                    |                                              |
|------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------|
| The attractive forces between $\text{CO}_2$ 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 =  $0.980 \times 10^{-18} \text{ J}$

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

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

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

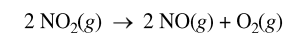
1 point is earned for the correct identification of the energy required to remove an electron from the valence shell (may be implicit).

1 point is earned for calculating the correct wavelength.

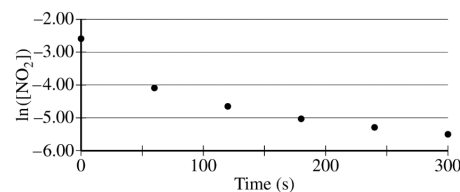
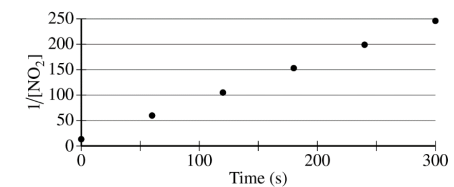
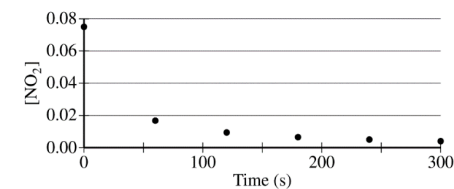
## 2019 SCORING GUIDELINES

## 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  $\text{NO}_2(\text{g})$ .

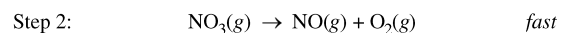
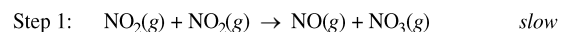
$$\text{rate} = k[\text{NO}_2]^2$$

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

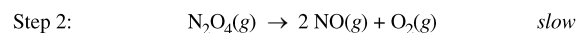


Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is  $\text{rate} = k[\text{NO}_2][\text{NO}_2] = k[\text{NO}_2]^2$ , which is consistent with the second-order rate law in part (b).

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



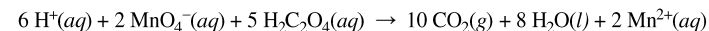
Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is  $\text{rate} = k[\text{N}_2\text{O}_4]$ . Because  $\text{N}_2\text{O}_4$  is an intermediate, it cannot appear in the rate law of the overall reaction. Because  $K_{eq} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$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



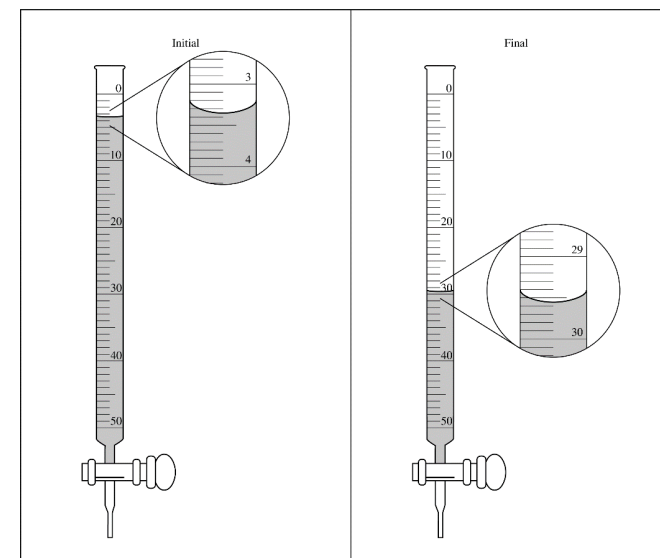
A student dissolved a 0.139 g sample of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , in water in an Erlenmeyer flask. Then the student titrated the  $\text{H}_2\text{C}_2\text{O}_4$  solution in the flask with a solution of  $\text{KMnO}_4$ , which has a dark purple color. The balanced chemical equation 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.

$\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  as the oxidation number of Mn changes from +7 to +2, indicating a gain of 5 electrons.

1 point is earned for the correct answer with justification.

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



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

1 point is earned for the correct answer.

## 2019 SCORING GUIDELINES

## Question 7 (continued)

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

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

1 point is earned for the correct answer.

The student proposes to perform another titration using a  $0.139\text{ g}$  sample of  $\text{H}_2\text{C}_2\text{O}_4$ , but this time using  $0.00143\text{ M}$   $\text{KMnO}_4(aq)$  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  $0.00143\text{ M}$  titrant solution is so diluted that volume of titrant needed to reach the end point would be much greater than the  $50\text{ mL}$  capacity of the buret.

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

2017

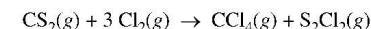
AP<sup>®</sup> CollegeBoard

# 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  $120^\circ\text{C}$  in a rigid  $25.0\text{ L}$  container.

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

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

$$n = \frac{PV}{RT} = \frac{0.40\text{ atm} \times 25.0\text{ L}}{0.08206\text{ (L} \cdot \text{atm})/(\text{mol} \cdot \text{K}) \times 393\text{ K}} = 0.31\text{ mol Cl}_2(g)$$

1 point is earned for the correct answer with supporting work.

(ii) How many grams of carbon disulfide,  $\text{CS}_2(g)$ , are needed to react completely with the  $\text{Cl}_2(g)$ ?

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

1 point is earned for using the correct mole ratio (may be implicit).

1 point is earned for the mass of  $\text{CS}_2$ .

(b) At  $30^\circ\text{C}$  the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at  $120^\circ\text{C}$ , the reaction occurs at an observable rate.

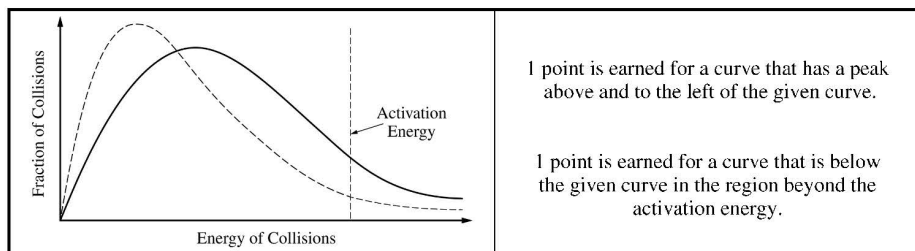
(i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at  $120^\circ\text{C}$ .

At the higher temperature the particles have a greater average kinetic energy than at the lower temperature. Thus there are more collisions with sufficient energy to overcome the activation energy.

1 point is earned for an appropriate explanation that includes a reference to molecular collisions.

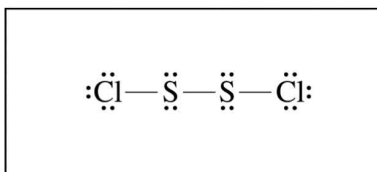
(ii) The graph below shows a distribution for the collision energies of reactant molecules at  $120^\circ\text{C}$ . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at  $30^\circ\text{C}$ .

## Question 1 (continued)



(c)  $\text{S}_2\text{Cl}_2$  is a product of the reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the  $\text{S}_2\text{Cl}_2$  molecule by drawing in all of the electron pairs.



See correct diagram above.

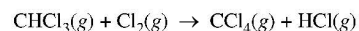
1 point is earned for a correctly drawn diagram.

(ii) What is the approximate value of the Cl–S–S bond angle in the  $\text{S}_2\text{Cl}_2$  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  $104^\circ$  and  $110^\circ$

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  $400^\circ\text{C}$ , 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  $70^\circ\text{C}$ , 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  $\text{CCl}_4$  molecules must be **stronger** than those among  $\text{HCl}$  molecules because the  $\text{CCl}_4$  condenses at a higher temperature than  $\text{HCl}$ .

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

## 2017 SCORING GUIDELINES

## 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.

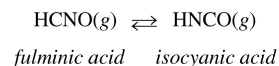
In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of  $-1$ . In the diagram on the right, the C atom has a formal charge of  $-1$  and the O atom has a formal charge of zero.

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

- (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  $\Delta H^\circ$  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  $\Delta H^\circ$ .

## 2017 SCORING GUIDELINES

## Question 2 (continued)

- (c) A student claims that  $\Delta S^\circ$  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.

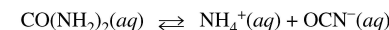
Isocyanic acid (HNCO) will be present in higher concentration.  
 $\Delta G^\circ$  is essentially equal to  $\Delta H^\circ$  because  $\Delta S^\circ$  is essentially zero, so  $\Delta G^\circ \approx -246 \text{ kJ/mol}_{\text{rxn}}$ , indicating the forward reaction is thermodynamically favorable.

Since  $\Delta G^\circ$  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  $\Delta G^\circ$  is a sufficient justification.)

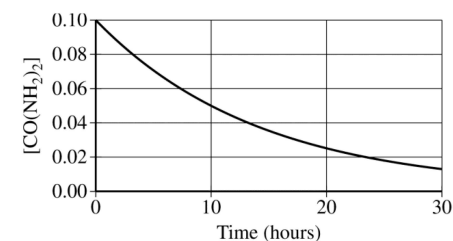
1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant,  $K$ .

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  $90^\circ\text{C}$ . 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                       |



## 2017 SCORING GUIDELINES

## Question 2 (continued)

(e) The student proposes that the rate law is  $rate = k[\text{CO}(\text{NH}_2)_2]$ .

(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.

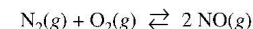
(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of  $\text{OH}^-(aq)$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

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.

AP<sup>®</sup> CHEMISTRY  
2017 SCORING GUIDELINES

## Question 3



At high temperatures,  $\text{N}_2(g)$  and  $\text{O}_2(g)$  can react to produce nitrogen monoxide,  $\text{NO}(g)$ , as represented by the equation above.

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

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

1 point is earned for a correct  $K_p$  expression.

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

|             |                                                                   |          |       |
|-------------|-------------------------------------------------------------------|----------|-------|
|             | $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$ |          |       |
| 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,  $\text{NO}(g)$ , can undergo further reactions to produce acids, such as  $\text{HNO}_2$ , a weak acid with a  $K_a$  of  $4.0 \times 10^{-4}$  and a  $\text{p}K_a$  of 3.40.

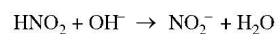
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M  $\text{HNO}_2(aq)$  and 0.100 M  $\text{NaOH}(aq)$ .

(i) Explain why the addition of 0.100 M  $\text{NaOH}(aq)$  to 0.100 M  $\text{HNO}_2(aq)$  can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the  $\text{NaOH}(aq)$  to the  $\text{HNO}_2(aq)$ .

## 2017 SCORING GUIDELINES

## Question 3 (continued)

NaOH will neutralize some of the  $\text{HNO}_2$  to produce  $\text{NO}_2^-$ . 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  $\text{HNO}_2$ (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  $\text{HNO}_2$  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  $\text{HNO}_2$  and  $\text{NO}_2^-$  (calculation not required).

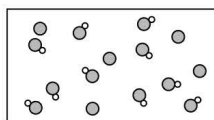
- (d) A second student makes a buffer by dissolving 0.100 mol of  $\text{NaNO}_2$ (s) in 100. mL of 1.00 M  $\text{HNO}_2$ (aq). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (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  $\text{HNO}_2$  and  $\text{NO}_2^-$  to react with added  $\text{H}^+$  or  $\text{OH}^-$  ions.

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

- (e) A new buffer is made using  $\text{HNO}_2$ (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.

●  $\text{HNO}_2$  molecule    ●  $\text{NO}_2^-$  ion



## 2017 SCORING GUIDELINES

## 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

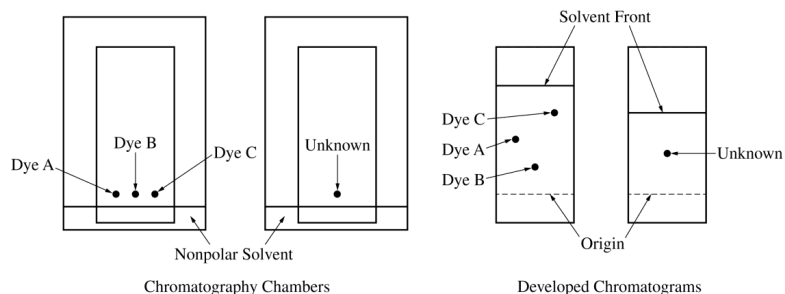
$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \Rightarrow \text{pH} = 3.40 + \log \frac{5}{10} \Rightarrow \text{pH} = 3.10$$

1 point is earned for the correct choice.

1 point is earned for a valid justification.

## 2017 SCORING GUIDELINES

## 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.

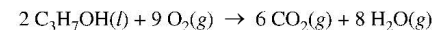
|                                                                                                                                               |                                                                                                  |
|----------------------------------------------------------------------------------------------------------------------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

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

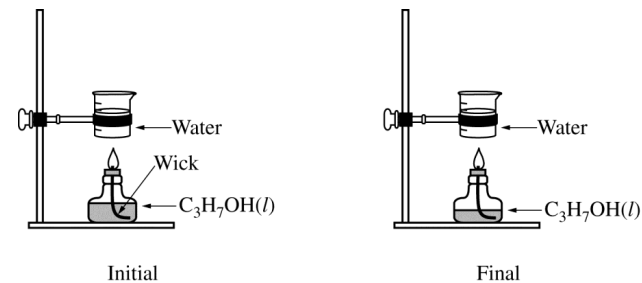
|                                                                                                                                                                                                                                                                                              |                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------|
| 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.<br>OR<br>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.)

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

**AP<sup>®</sup> CHEMISTRY**  
**2017 SCORING GUIDELINES**

**Question 5 (continued)**

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

|                                                                                                                                                                                                                                                         |                                                                                                                                                                                                      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $1 \text{ mol C}_3\text{H}_7\text{OH} \times \frac{60.09 \text{ g C}_3\text{H}_7\text{OH}}{1 \text{ mol C}_3\text{H}_7\text{OH}} \times \frac{15.2 \text{ kJ}}{0.55 \text{ g C}_3\text{H}_7\text{OH}} = 1661 \text{ kJ}$ $= 1.7 \times 10^3 \text{ kJ}$ | <p>1 point is earned for the correct amount of heat released.</p> <p>1 point is earned for reporting the answer to the appropriate number of significant figures based on the experimental data.</p> |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

- (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.

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

**2017 SCORING GUIDELINES**

**Question 6**

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

- (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  $25^\circ\text{C}$ .

|                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (x)(2x)^2 = 4x^3$ $x = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.65 \times 10^{-4} \text{ M} = [\text{Mg}^{2+}] = [\text{Mg}(\text{OH})_2]$ $0.100 \text{ L} \times \frac{1.65 \times 10^{-4} \text{ mol}}{1 \text{ L}} \times \frac{58.32 \text{ g Mg}(\text{OH})_2}{1 \text{ mol Mg}(\text{OH})_2} = 9.6 \times 10^{-4} \text{ g Mg}(\text{OH})_2$ | <p>1 point is earned for calculating the solubility of <math>\text{Mg}(\text{OH})_2</math>.</p> <p>1 point is earned for calculating the correct mass based on the solubility of <math>\text{Mg}(\text{OH})_2</math>.</p> |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

- (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.

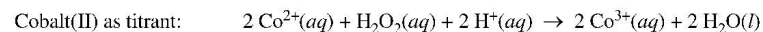
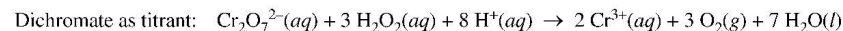
| Reaction                                                                      | Lattice Energy (kJ/mol) |
|-------------------------------------------------------------------------------|-------------------------|
| $\text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(g) + 2 \text{ OH}^-(g)$ | 2900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

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>The <math>\text{Sr}^{2+}</math> ion is larger than the <math>\text{Mg}^{2+}</math> 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 <math>\text{Mg}^{2+}</math> and <math>\text{OH}^-</math> is shorter than the distance between <math>\text{Sr}^{2+}</math> and <math>\text{OH}^-</math>, the attractive forces in <math>\text{Mg}(\text{OH})_2</math> are stronger and, therefore, its lattice energy is greater.</p> | <p>1 point is earned for the correct comparison of cation sizes.</p> <p>1 point is earned for indicating that smaller interionic distances lead to a greater lattice energy.</p> |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

## 2017 SCORING GUIDELINES

## Question 7

A student wants to determine the concentration of  $\text{H}_2\text{O}_2$  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  $E^\circ$  values for the systems related to the titrations above are given in the following table.

| Half-Reaction                                                                                                           | $E^\circ$ (V)<br>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)  $E^\circ$  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 $E^\circ$ values. |
|------------------------------------------|-------------------------------------------------------------|

(ii)  $E^\circ$  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 $E^\circ$ values. |
|--------------------------------------------|-------------------------------------------------------------|

## 2017 SCORING GUIDELINES

## Question 7 (continued)

(b) Based on the calculated values of  $E^\circ$ , 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  $E^\circ$  is positive, which means that the reaction is thermodynamically favorable.

OR

$\Delta G^\circ = -nFE^\circ$  and  $n$ ,  $F$ , and  $E^\circ$  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  $E^\circ$  or a negative  $\Delta G^\circ$  is required.

(ii) Calculate the value of  $\Delta G^\circ$ , 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  $\Delta G^\circ$ .