

**AP<sup>®</sup> CHEMISTRY**  
**2013 SCORING GUIDELINES**

**Question 1**  
**(10 points)**

Answer the following questions about the solubility of some fluoride salts of alkaline earth metals.

- (a) A student prepares 100. mL of a saturated solution of  $\text{MgF}_2$  by adding 0.50 g of solid  $\text{MgF}_2$  to 100. mL of distilled water at  $25^\circ\text{C}$  and stirring until no more solid dissolves. (Assume that the volume of the undissolved  $\text{MgF}_2$  is negligibly small.) The saturated solution is analyzed, and it is determined that  $[\text{F}^-]$  in the solution is  $2.4 \times 10^{-3} \text{ M}$ .

- (i) Write the chemical equation for the dissolving of solid  $\text{MgF}_2$  in water.

$\text{MgF}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{F}^-(aq)$	1 point is earned for the correct equation.
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- (ii) Calculate the number of moles of  $\text{MgF}_2$  that dissolved.

$\frac{2.4 \times 10^{-3} \text{ mol F}^-}{1.0 \text{ L}} \times 0.100 \text{ L} \times \frac{1 \text{ mol MgF}_2}{2 \text{ mol F}^-} = 1.2 \times 10^{-4} \text{ mol MgF}_2$	<p>1 point is earned for the correct calculation of moles from concentration.</p> <p>1 point is earned for the correct stoichiometry.</p>
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- (iii) Determine the value of the solubility-product constant,  $K_{sp}$ , for  $\text{MgF}_2$  at  $25^\circ\text{C}$ .

$[\text{Mg}^{2+}] = \frac{1}{2} [\text{F}^-] = \frac{1}{2} (2.4 \times 10^{-3} \text{ M}) = 1.2 \times 10^{-3} \text{ M}$ $K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2 = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2$ $= 6.9 \times 10^{-9}$	<p>1 point is earned for the correct value of <math>[\text{Mg}^{2+}]</math></p> <p>1 point is earned for the correct setup for determining the value of <math>K_{sp}</math>.</p> <p>1 point is earned for the correct value of <math>K_{sp}</math>.</p>
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**Question 1 (continued)**

- (b) A beaker contains 500. mL of a solution in which both  $\text{Ca}^{2+}(\text{aq})$  and  $\text{Ba}^{2+}(\text{aq})$  are present at a concentration of 0.10 M at 25°C. A student intends to separate the ions by adding 0.20 M NaF solution one drop at a time from a buret. At 25°C the value of  $K_{sp}$  for  $\text{CaF}_2$  is  $3.5 \times 10^{-11}$ ; the value of  $K_{sp}$  for  $\text{BaF}_2$  is  $1.8 \times 10^{-6}$ .

- (i) Which salt will precipitate first,  $\text{CaF}_2$  or  $\text{BaF}_2$  ? Justify your answer.

$\text{CaF}_2$ will precipitate first. Its $K_{sp}$ value is smaller, thus the ion-concentration product $[\text{Ca}^{2+}][\text{F}^-]^2$ will be the first to exceed the $K_{sp}$ value.	1 point is earned for the correct choice with its justification.
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For parts (b)(ii) and (b)(iii) below, assume that the addition of the NaF solution does not significantly affect the total volume of the liquid in the beaker.

- (ii) Calculate the minimum concentration of  $\text{F}^-(\text{aq})$  necessary to initiate precipitation of the salt selected in part (b)(i).

$K_{sp} = 3.5 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.10)[\text{F}^-]^2$ $3.5 \times 10^{-10} = [\text{F}^-]^2$ $[\text{F}^-] = \sqrt{3.5 \times 10^{-10}} = 1.9 \times 10^{-5} \text{ M}$	1 point is earned for the correct value of $[\text{F}^-]$ .
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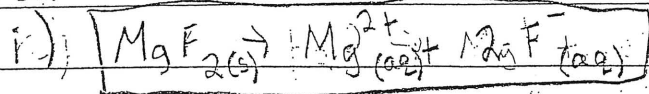
- (iii) Calculate the minimum volume of 0.20 M NaF that must be added to the beaker to initiate precipitation of the salt selected in part (b)(i).

Assuming that the volume of added $\text{NaF}(\text{aq})$ is negligible, the total volume of the solution at the point of precipitation is 500. mL. $(0.20 \text{ M})(V) = (1.9 \times 10^{-5} \text{ M})(0.500 \text{ L})$ $V = 4.7 \times 10^{-5} \text{ L (or } 4.8 \times 10^{-5} \text{ L)}$ $= 4.7 \times 10^{-2} \text{ mL (or } 4.8 \times 10^{-2} \text{ mL)}$	1 point is earned for the correct volume.
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- (c) There are several ways to dissolve salts that have limited solubility. Describe one procedure to redissolve the precipitate formed in part (b).

Valid procedures include adding water, adding acid ( $\text{H}^+$ ), heating (i.e., increasing the temperature), and any valid statement that implies a shifting of the equilibrium toward the products side of the dissolution equation.	1 point is earned for a description of a valid procedure.
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1) a)



$$ii.) \quad \boxed{1 \text{ L} \left| \frac{2.4 \times 10^{-3} \text{ mol F}^{-}}{1 \text{ L}} \right| \frac{1 \text{ mol MgF}_2}{2 \text{ mol F}^{-}} = 1.2 \times 10^{-4} \text{ moles MgF}_2 \text{ dissolved}}$$

$$iii.) \quad K_{sp} = [\text{Mg}^{2+}][\text{F}^{-}]^2$$

$$[\text{Mg}^{2+}] = \frac{1}{2} [\text{F}^{-}] = \frac{1}{2} (2.4 \times 10^{-3}) = .0012 \text{ M}$$

$$(.0012)(2.4 \times 10^{-3})^2 = \boxed{6.9 \times 10^{-9} = K_{sp} @ 25^{\circ}\text{C}}$$

b.)

i) The  $\text{CaF}_2$  will precipitate first because its  $K_{sp}$  ( $3.5 \times 10^{-11}$ ) is smaller than  $\text{BaF}_2$ 's  $K_{sp}$  ( $1.8 \times 10^{-6}$ ), meaning that the  $\text{CaF}_2$  is less soluble than  $\text{BaF}_2$ , so it will precipitate out first with the addition of  $\text{F}^{-}$  ions.

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

$$ii.) \quad 3.5 \times 10^{-11} = .1 \text{ M} \times x^2$$

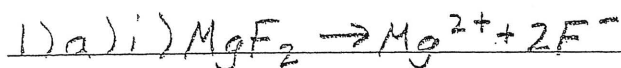
$$\frac{3.5 \times 10^{-11}}{.1} = x^2 = 3.5 \times 10^{-10} \quad x = \sqrt{3.5 \times 10^{-10}} = \boxed{1.9 \times 10^{-5} \text{ M}}$$

$$iii.) \quad \boxed{1.9 \times 10^{-5} \text{ mol} / .5 \text{ L} = 9.5 \times 10^{-6} \text{ moles} \quad | \quad 1 \text{ L NaF} = 4.75 \times 10^{-5} \text{ L} \quad | \quad .2 \text{ mol}}$$

$$\boxed{4.75 \times 10^{-5} \text{ L} / 1000 \text{ mL} = \text{a minimum of } .048 \text{ mL of NaF must be added}}$$

c) If you add more water (distilled  $\text{H}_2\text{O}$ ) to the solution, the molarities will all decrease, therefore allowing more  $\text{CaF}_2$  to dissolve, re-dissolving the precipitate formed in part b.

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ii)  $.50\text{g MgF}_2 \cdot \frac{\text{mol}}{62.3\text{g}} = .0080\text{mol MgF}_2$

iii)  $K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2 = \left[\frac{2.4 \times 10^{-3}}{2}\right][2.4 \times 10^{-3}]^2 = 6.9 \times 10^{-9}$

b) i)  $\text{CaF}_2$  will precipitate first because the  $K_{sp}$  for  $\text{CaF}_2$  is much smaller than the value for the  $K_{sp}$  of  $\text{BaF}_2$ . This means that  $\text{BaF}_2$  is more likely to dissociate than precipitate.  $\text{CaF}_2$  is more likely to precipitate, so it will precipitate first.

ii)  $3.5 \times 10^{-11} = [1.0][\text{F}^-]^2$

$[\text{F}^-]^2 = 3.5 \times 10^{-10}$

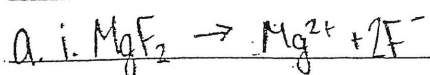
$[\text{F}^-] = 1.9 \times 10^{-5}\text{M}$

iii)  $.5\text{L} \cdot \frac{1.9 \times 10^{-5}\text{mol}}{\text{L}} = 9.5 \times 10^{-6}\text{mol F}^-$

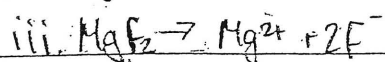
$9.5 \times 10^{-6}\text{mol} \cdot \frac{\text{L}}{.20\text{mol}} = 4.8 \times 10^{-5}\text{L}$

c) Heat the solution while stirring until the solid  $\text{CaF}_2$  is able to dissociate.

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ii.  $n_{\text{MgF}_2} = n_{\text{F}^-} \times \frac{1}{2} = CV \times \frac{1}{2} = (2.4 \times 10^{-3}) \left( \frac{100}{1000} \right) \times \frac{1}{2} = \boxed{1.2 \times 10^{-4} \text{ mol}}$



I    Y            0    0

C   -x           +x   +2x

E                x    2x

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

$= (x)(2x)^2$

$= (1.2 \times 10^{-4})(2.4 \times 10^{-3})^2$

$\boxed{K_{sp} = 6.91 \times 10^{-10}}$

b. i.  $\text{BaF}_2$  will precipitate first because it has a higher molar solubility than  $\text{CaF}_2$

ii.  $K_{sp} = [\text{Ba}^{2+}] \times [\text{F}^-]^2$

$1.8 \times 10^{-6} = (x)(2x)^2$

$1.8 \times 10^{-6} = 4x^3$

$x = .00766 \text{ M}$

$\boxed{[\text{F}^-] = \frac{x}{2} = .00383 \text{ M}}$

iii.  $CV = CV$

$(.2)(500) = (.00383)(500 + x)$

$\boxed{x = 25,610. \text{ mL}}$

c. Dilute the solution with enough water to lower the  $[\text{F}^-]$  concentration enough for the precipitate to redissolve

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## 2013 SCORING COMMENTARY

### Question 1

#### Overview

This equilibrium question focused on solubility chemistry and consists of three components: foundational knowledge regarding solubility chemistry, selective precipitation, and factors that can influence the solubility equilibrium. In part (a)(i) students wrote a chemical equation to represent the solubility reaction. Part (a)(ii) required stoichiometric knowledge and the ability to manipulate concentration calculations. In part (a)(iii) students used knowledge of solubility-product chemistry to calculate the equilibrium constant ( $K_{sp}$ ) for the dissolution reaction. In part (b)(i) students judged the relative solubility of salts based on the values of solubility product constants. In part (b)(ii) students calculated the minimum  $F^-$  concentration necessary to initiate precipitation of  $CaF_2$  using the solubility-product constant and a given value for  $[Ca^{2+}]$ . In part (b)(iii) students calculated the volume of  $NaF$  solution at a given concentration to be added to start the precipitation of  $CaF_2$ . In part (c) students described a process, based on knowledge of what factors influence equilibria, to redissolve the precipitate formed in part (b).

#### Sample: 1A

**Score: 10**

This excellent response earned all 10 points. In part (a)(i) the chemical equation earned 1 point. Mass and charge balance are clearly shown. The phase symbols are shown in this equation, but are not required for the point. Part (a)(ii) earned 2 points. Part (a)(iii) earned 3 points. The first point was earned for showing the  $K_{sp}$  expression consistent with the chemical equation written in part (a)(i). The second point was earned for calculating the equilibrium  $[Mg^{2+}]$ . The third point was earned for completing the calculation of  $K_{sp}$  using the values in the student's work and using the  $[F^-]$  given in the question appropriately in the problem. One point was earned in part (b)(i) for stating that the  $CaF_2$  is the first to precipitate with the justification that the  $K_{sp}$  of  $CaF_2$  is less than the  $K_{sp}$  of  $BaF_2$ . The calculation of the minimum  $[F^-]$  earned 1 point in part (b)(ii). One point was earned in part (b)(iii) for the correct dilution calculation using the answer from part (b)(ii). One point was earned in part (c) for stating that the addition of distilled water allows more  $CaF_2$  to dissolve in the solution.

#### Sample: 1B

**Score: 8**

This response earned 8 points. The two points in part (a)(ii) were not earned because the student solved for the number of moles of  $MgF_2$  starting from the number of grams of  $MgF_2$  given in the question. This method determines the total number of moles of  $MgF_2$ , not the number of moles dissolved in the solution.

#### Sample: 1C

**Score: 6**

This response earned 6 points. The second point for part (a)(iii) was not earned because the student incorrectly used the value of moles from part (a)(ii) as the  $[Mg^{2+}]$ . The third point for part (a)(iii) was earned for completing the calculation of  $K_{sp}$  using the values in the student's work and using the  $[F^-]$  given in the question appropriately in the problem. The point in part (b)(i) was not earned because student  $BaF_2$  was incorrectly selected as the solid that would precipitate first. The point for part (b)(ii) was not earned because the student did the calculation for  $BaF_2$  as a result of selecting  $BaF_2$  as the compound that precipitates first, which is consistent with the student's choice in part (b)(i). However, the information

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**Question 1 (continued)**

about the  $[\text{Ba}^{2+}]$  given in the problem was not included. A second reason this point was not earned is for the incorrect stoichiometry used to calculate the  $[\text{F}^-]$ . The point for part (b)(iii) was not earned. A correct method for calculating dilutions was used; however, the variable  $x$  was incorrectly used in the calculations. The point was earned for part (c).