AP® 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 MgF_2 by adding 0.50 g of solid MgF_2 to 100. mL of distilled water at 25°C and stirring until no more solid dissolves. (Assume that the volume of the undissolved MgF_2 is negligibly small.) The saturated solution is analyzed, and it is determined that $[F^-]$ in the solution is $2.4 \times 10^{-3}\ M$.

(i) Write the chemical equation for the dissolving of solid MgF_2 in water.

$MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ F^-(aq)$	1 point is earned for the correct equation.

(ii) Calculate the number of moles of MgF_2 that dissolved.

$\frac{2.4 \times 10^{-3}\ \text{mol}\ F^-}{1.0\ \text{L}} \times 0.100\ \text{L} \times \frac{1\ \text{mol}\ MgF_2}{2\ \text{mol}\ F^-} = 1.2 \times 10^{-4}\ \text{mol}\ MgF_2$	1 point is earned for the correct calculation of moles from concentration. 1 point is earned for the correct stoichiometry.

(iii) Determine the value of the solubility-product constant, K_{sp}, for MgF_2 at 25°C.

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

Question 1 (continued)

(b) A beaker contains 500. mL of a solution in which both $Ca^{2+}(aq)$ and $Ba^{2+}(aq)$ 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 CaF_2 is 3.5×10^{-11}; the value of K_{sp} for BaF_2 is 1.8×10^{-6}.

(i) Which salt will precipitate first, CaF_2 or BaF_2 ? Justify your answer.

CaF_2 will precipitate first. Its K_{sp} value is smaller, thus the ion-concentration product $[Ca^{2+}][F^-]^2$ will be the first to exceed the K_{sp} value.	1 point is earned for the correct choice with its justification.

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 $F^-(aq)$ necessary to initiate precipitation of the salt selected in part (b)(i).

$K_{sp} = 3.5 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (0.10)[F^-]^2$ $3.5 \times 10^{-10} = [F^-]^2$ $[F^-] = \sqrt{3.5 \times 10^{-10}} = 1.9 \times 10^{-5}\ M$	1 point is earned for the correct value of $[F^-]$.

(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 $NaF(aq)$ is negligible, the total volume of the solution at the point of precipitation is 500. mL. $(0.20\ M)(V) = (1.9 \times 10^{-5}\ M)(0.500\ \text{L})$ $V = 4.7 \times 10^{-5}\ \text{L}$ (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.

(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 (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.

1) a)

i) $MgF_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2F^-_{(aq)}$

ii) $1\,L \left| \frac{2.4 \times 10^{-3}\ mol\ F^-}{1\,L} \right| \left| \frac{1\ mol\ MgF_2}{2\ mol\ F^-} \right| = 1.2 \times 10^{-4}$ moles MgF_2 dissolved

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

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

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

b)

i) The CaF_2 will precipitate first because its K_{sp} (3.5×10^{-11}) is smaller than BaF_2's K_{sp} (1.8×10^{-6}), meaning that the CaF_2 is less soluble than BaF_2, so it will precipitate out first with the addition of F^- ions.

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

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

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

iii) $\frac{1.9 \times 10^{-5}\ mol}{1\,L} | .5\,L = 9.5 \times 10^{-6}$ moles $\left| \frac{1\,L\ NaF}{.2\ mol} \right. = 4.75 \times 10^{-5}\,L$

$4.75 \times 10^{-5}\,L \left| \frac{1000\ mL}{1\,L} \right. =$ a minimum of .048 mL of NaF must be added

c) If you add more water (distilled H_2O) to the solution, the molarities will all decrease, therefore allowing more CaF_2 to dissolve, re-dissolving the precipitate formed in part b.

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1) a) i) $MgF_2 \rightarrow Mg^{2+} + 2F^-$

ii) $.50\text{g } MgF_2 \cdot \frac{\text{mol}}{62.3\text{g}} = .0080\text{mol } MgF_2$

iii) $K_{sp} = [Mg^{2+}][F^-]^2 = \left[\frac{2.4\times10^{-3}}{2}\right]\left[2.4\times10^{-3}\right]^2 = 6.9\times10^{-9}$

b) i) CaF_2 will precipitate first because the Ksp for CaF_2 is much smaller than the value for the Ksp of BaF_2. This means that BaF_2 is more likely to dissociate then precipitate. CaF_2 is more likely to precipitate, so it will precipitate first.

ii) $3.5\times10^{-11} = [.10][F^-]^2$

$[F^-]^2 = 3.5\times10^{-10}$

$[F^-] = 1.9\times10^{-5}\text{M}$

iii) $.5\text{L} \cdot \frac{1.9\times10^{-5}\text{mol}}{\text{L}} = 9.5\times10^{-6}\text{mol } F^-$

$9.5\times10^{-5}\text{mol} \cdot \frac{\text{L}}{.20\text{mol}} = 4.8\times10^{-5}\text{L}$

c) Heat the solution while stiring until the solid CaF_2 is able to dissociate.

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1C

a. i. $MgF_2 \rightarrow Mg^{2+} + 2F^-$

ii. $n_{MgF_2} = n_{F^-} \times \frac{1}{2} = CV \times \frac{1}{2} = (2.4\times10^{-3})\left(\frac{100}{1000}\right) \times \frac{1}{2} = \boxed{1.2\times10^{-4}\ mol}$

iii. $MgF_2 \rightarrow Mg^{2+} + 2F^-$

I	Y	0	0
C	-x	+x	+2x
E		x	2x

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

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

$= (1.2\times10^{-4})(2.4\times10^{-3})^2$

$\boxed{K_{sp} = 6.91\times10^{-10}}$

b. i. BaF_2 will precipitate first because it has a higher molar solubility than CaF_2

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

$1.8\times10^{-6} = (x)(2x)^2$

$1.8\times10^{-6} = 4x^3$

$x = .00766\ M$

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

iii. $CV = CV$

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

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

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

AP® CHEMISTRY
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

Question 1 (continued)

about the [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 [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).