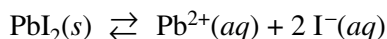


**AP[®] CHEMISTRY
2006 SCORING GUIDELINES**

Question 1

1. Answer the following questions that relate to solubility of salts of lead and barium.

- (a) A saturated solution is prepared by adding excess $\text{PbI}_2(s)$ to distilled water to form 1.0 L of solution at 25°C . The concentration of $\text{Pb}^{2+}(aq)$ in the saturated solution is found to be $1.3 \times 10^{-3} M$. The chemical equation for the dissolution of $\text{PbI}_2(s)$ in water is shown below.



- (i) Write the equilibrium-constant expression for the equation.

$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2$	One point is earned for the correct expression.
---	---

- (ii) Calculate the molar concentration of $\text{I}^{-}(aq)$ in the solution.

By stoichiometry, $[\text{I}^{-}] = 2 \times [\text{Pb}^{2+}]$, thus $[\text{I}^{-}] = 2 \times (1.3 \times 10^{-3}) = 2.6 \times 10^{-3} M$	One point is earned for the correct concentration.
--	--

- (iii) Calculate the value of the equilibrium constant, K_{sp} .

$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = (1.3 \times 10^{-3})(2.6 \times 10^{-3})^2$ $= 8.8 \times 10^{-9}$	One point is earned for a value of K_{sp} that is consistent with the answers in parts (a)(i) and (a)(ii).
--	--

- (b) A saturated solution is prepared by adding $\text{PbI}_2(s)$ to distilled water to form 2.0 L of solution at 25°C . What are the molar concentrations of $\text{Pb}^{2+}(aq)$ and $\text{I}^{-}(aq)$ in the solution? Justify your answer.

The molar concentrations of $\text{Pb}^{2+}(aq)$ and $\text{I}^{-}(aq)$ would be the same as in the 1.0 L solution in part (a) (i.e., $1.3 \times 10^{-3} M$ and $2.6 \times 10^{-3} M$, respectively). The concentrations of solute particles in a saturated solution are a function of the constant, K_{sp} , which is independent of volume.	One point is earned for the concentrations (or stating they are the same as in the solution described in part (a)) and justification.
--	---

AP[®] CHEMISTRY
2006 SCORING GUIDELINES

Question 1 (continued)

- (c) Solid NaI is added to a saturated solution of PbI_2 at 25°C . Assuming that the volume of the solution does not change, does the molar concentration of $\text{Pb}^{2+}(\text{aq})$ in the solution increase, decrease, or remain the same? Justify your answer.

<p>$[\text{Pb}^{2+}]$ will decrease.</p> <p>The $\text{NaI}(\text{s})$ will dissolve, increasing $[\text{I}^-]$; more $\text{I}^-(\text{aq})$ then combines with $\text{Pb}^{2+}(\text{aq})$ to precipitate $\text{PbI}_2(\text{s})$ so that the ion product $[\text{Pb}^{2+}][\text{I}^-]^2$ will once again attain the value of 8.8×10^{-9} (K_{sp} at 25°C).</p>	<p>One point is earned for stating that $[\text{Pb}^{2+}]$ will decrease.</p> <p>One point is earned for justification (can involve a Le Chatelier argument).</p>
--	--

- (d) The value of K_{sp} for the salt BaCrO_4 is 1.2×10^{-10} . When a 500. mL sample of $8.2 \times 10^{-6} M$ $\text{Ba}(\text{NO}_3)_2$ is added to 500. mL of $8.2 \times 10^{-6} M$ Na_2CrO_4 , no precipitate is observed.

- (i) Assuming that volumes are additive, calculate the molar concentrations of $\text{Ba}^{2+}(\text{aq})$ and $\text{CrO}_4^{2-}(\text{aq})$ in the 1.00 L of solution.

<p>New volume = 500. mL + 500. mL = 1.000 L, therefore $[\text{Ba}^{2+}]$ in 1.000 L is one-half its initial value:</p> $[\text{Ba}^{2+}] = \frac{500. \text{ mL}}{1,000. \text{ mL}} \times (8.2 \times 10^{-6} M) = 4.1 \times 10^{-6} M$ $[\text{CrO}_4^{2-}] = \frac{500. \text{ mL}}{1,000. \text{ mL}} \times (8.2 \times 10^{-6} M) = 4.1 \times 10^{-6} M$	<p>One point is earned for the correct concentration.</p>
---	---

- (ii) Use the molar concentrations of $\text{Ba}^{2+}(\text{aq})$ ions and $\text{CrO}_4^{2-}(\text{aq})$ ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

<p>The product $Q = [\text{Ba}^{2+}][\text{CrO}_4^{2-}]$</p> $= (4.1 \times 10^{-6} M)(4.1 \times 10^{-6} M)$ $= 1.7 \times 10^{-11}$ <p>Because $Q = 1.7 \times 10^{-11} < 1.2 \times 10^{-10} = K_{sp}$, no precipitate forms.</p>	<p>One point is earned for calculating a value of Q that is consistent with the concentration values in part (d)(i).</p> <p>One point is earned for using Q to explain why no precipitate forms.</p>
---	--

① (A) (i) $K_{sp} = [Pb^{2+}][I^-]^2$
 (ii) $[I^-] = 2[Pb^{2+}] = 0.0026 M$
 (iii) $K_{sp} = [x][2x]^2 = 4x^3$
 $4x^3 | x = 1.3 \times 10^{-3} = 8.79 \times 10^{-9} \rightarrow 8.8 \times 10^{-9}$

(B) $K_{sp} = 8.79 \times 10^{-9}$
 $[Pb^{2+}] = 1.3 \times 10^{-3}$ $[I^-] = 2.6 \times 10^{-3}$

The concentrations at equilibrium do not change because the K_{sp} is constant for all volumes of solution. This occurs because the amount of compound for saturation for PbI_2 is double that in 2L than in 1L.

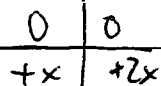
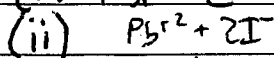
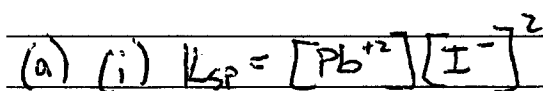
(C) Due to the Common Ion effect the excess I^- ions will upset the equilibrium forcing Pb^{2+} to precipitate out of solution. The concentration of Pb^{2+} must DECREASE in order for equilibrium to remain constant.

(D) (i) $[Ba^{2+}] = \frac{(8.2 \times 10^{-6})(0.5)}{0.5 + 0.5} = 4.1 \times 10^{-6} M$
 $[CrO_4^{2-}] = \frac{(8.2 \times 10^{-6})(0.5)}{0.5 + 0.5} = 4.1 \times 10^{-6} M$

(ii) $Q = [Ba^{2+}][CrO_4^{2-}] = (4.1 \times 10^{-6})^2$
 $= 1.681 \times 10^{-11}$ $1.68 \times 10^{-11} < 1.2 \times 10^{-10}$
 $Q = 1.681 \times 10^{-11}$ $K = 1.2 \times 10^{-10}$ $Q < K$

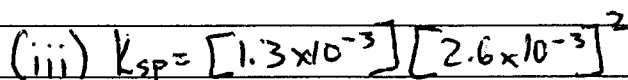
There is no precipitate because the Q for the reaction is less than the K . As 1.2×10^{-10} is larger than the Q of 1.681×10^{-11} no precipitate forms because there is not an excess of ions that would require precipitation due to saturation of ions.

GO ON TO THE NEXT PAGE.



$x = 1.3 \times 10^{-3}$ $2x = 2.6 \times 10^{-3}$

$[I^-] = 2.6 \times 10^{-3} M$



~~$K_{sp} = 8.8 \times 10^{-9}$~~

$K_{sp} = 8.8 \times 10^{-9}$

(b) $[Pb^{+2}] = 1.3 \times 10^{-3} M$ and $[I^-] = 2.6 \times 10^{-3} M$ because that is the largest concentration that can exist in a solution until the solution is supersaturated. $8.8 \times 10^{-9} = [x][2x]^2 = 4x^3$
 $x = 1.3 \times 10^{-3}$ and $2x = 2.6 \times 10^{-3}$

(c) ~~Decreases~~ $[Pb^{+2}]$ remains the same because more I^- ions will not affect the concentration of lead ions.

(d) (i)

$M_1 V_1 = M_2 V_2$

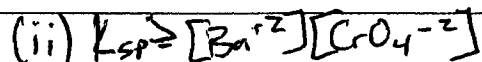
$(8.2 \times 10^{-6})(.5) = (M_2)(1)$

$M_1 V_1 = M_2 V_2$

$(8.2 \times 10^{-6})(.5) = (M_2)(1)$

$[Ba^{+2}] = 4.1 \times 10^{-6} M$

$[CrO_4^{-2}] = 4.1 \times 10^{-6} M$



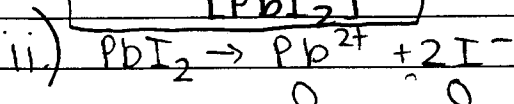
$1.2 \times 10^{-10} \geq [4.1 \times 10^{-6}][4.1 \times 10^{-6}]$

$1.2 \times 10^{-10} > 1.7 \times 10^{-11}$

Since K_{sp} is larger than the value of the K_{sp} expression, ~~more~~ a larger concentration can still be soluble. If the value of the K_{sp} expression was greater than 1.2×10^{-10} , a precipitate would form.

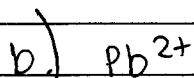
GO ON TO THE NEXT PAGE.

1 a) i)
$$K = \frac{[Pb^{2+}][I^-]^2}{[PbI_2]}$$



$$-1.3 \times 10^{-3} \quad +1.3 \times 10^{-3} \quad +2(1.3 \times 10^{-3})$$

$$2.6 \times 10^{-3} M = [I^-]$$



$$(1.3 \times 10^{-3} M)(1.0 L) = 1.3 \times 10^{-3} \text{ mol}$$

$$\frac{1.3 \times 10^{-3} \text{ mol}}{2 L} =$$

$$[Pb^{2+}] = 6.5 \times 10^{-4} M$$

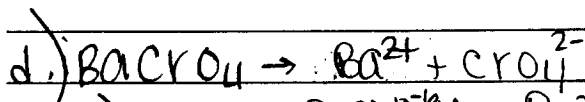


$$(2.6 \times 10^{-3})(1.0 L) = 2.6 \times 10^{-3} \text{ mol}$$

$$\frac{2.6 \times 10^{-3} \text{ mol}}{2 L} =$$

$$[I^-] = 1.3 \times 10^{-3} M$$

c.) The concentration of Pb^{2+} decreases since now there is an increase of I^- present in the solution without altering the volume.



i)

$$8.2 \times 10^{-6} M \quad 8.2 \times 10^{-6} M$$

$$\times 0.5 L \quad \times 0.5 L$$

$$\frac{4.1 \times 10^{-6} \text{ mol}}{1.0 L} \quad \frac{4.1 \times 10^{-6} \text{ mol}}{1.0 L}$$

$$[Ba^{2+}] + [CrO_4^{2-}] = 4.1 \times 10^{-6} M$$

ii) $Q = (4.1 \times 10^{-6})^2$

$Q = 1.7 \times 10^{-11} \quad K_{sp} = 1.2 \times 10^{-10}$

$1.7 \times 10^{-11} < 1.2 \times 10^{-10}$

$Q < K$

A precipitate cannot occur in the reaction present in part (d) because the calculated value of Q is less than the given value of K_{sp} .

GO ON TO THE NEXT PAGE.

AP[®] CHEMISTRY
2006 SCORING COMMENTARY

Question 1

Overview

This was a required equilibrium problem designed to assess students' understanding of solubility and principles of solubility equilibrium. Students were expected to write an expression for the K_{sp} from the solubility equation, determine the stoichiometric relationship between concentrations of ions, and calculate the value of the K_{sp} .

They were asked to assess the effect of different volumes of solution on the concentrations of ions in a saturated solution and the effect of adding a soluble salt containing a common ion. The last part of the question assessed students' ability to calculate concentrations of ions from dilution data and to calculate and interpret the value of Q in comparison to K_{sp} .

Sample: 1A

Score: 9

This response earned all 9 points: 1 point for part (a)(i), 1 point for part (a)(ii), 1 point for part (a)(iii), 1 point for part (b), 2 points for part (c), 1 point for part (d)(i), and 2 points for part (d)(ii).

Sample: 1B

Score: 7

All of the points were earned in parts (a), (b), and (d). The points were not earned in part (c) because the student does not show that an increase in $[I^-]$ results in a decrease in $[Pb^{2+}]$.

Sample: 1C

Score: 5

The point was not earned in part (a)(i) because solid PbI_2 is included in the expression. Part (a)(iii) is not attempted. The point was not earned in part (b) because the concentrations are halved. In part (c) 1 point was earned for stating that $[Pb^{2+}]$ decreases; however, the justification is insufficient to have earned the second point. All 3 points were earned in part (d).