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 $PbI_2(s)$ to distilled water to form 1.0 L of solution at 25°C. The concentration of $Pb^{2+}(aq)$ in the saturated solution is found to be 1.3×10^{-3} M. The chemical equation for the dissolution of $PbI_2(s)$ in water is shown below.

$$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\, I^-(aq)$$

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

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

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

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

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

$K_{sp} = [Pb^{2+}][I^-]^2 = (1.3 \times 10^{-3})(2.6 \times 10^{-3})^2$ $= 8.8 \times 10^{-9}$	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 $PbI_2(s)$ to distilled water to form 2.0 L of solution at 25°C. What are the molar concentrations of $Pb^{2+}(aq)$ and $I^-(aq)$ in the solution? Justify your answer.

The molar concentrations of $Pb^{2+}(aq)$ and $I^-(aq)$ 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.

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 $Pb^{2+}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer.

$[Pb^{2+}]$ will decrease. The $NaI(s)$ will dissolve, increasing $[I^-]$; more $I^-(aq)$ then combines with $Pb^{2+}(aq)$ to precipitate $PbI_2(s)$ so that the ion product $[Pb^{2+}][I^-]^2$ will once again attain the value of 8.8×10^{-9} (K_{sp} at 25°C).	One point is earned for stating that $[Pb^{2+}]$ will decrease. One point is earned for justification (can involve a Le Chatelier argument).

(d) The value of K_{sp} for the salt $BaCrO_4$ is 1.2×10^{-10}. When a 500. mL sample of 8.2×10^{-6} M $Ba(NO_3)_2$ is added to 500. mL of 8.2×10^{-6} M Na_2CrO_4, no precipitate is observed.

(i) Assuming that volumes are additive, calculate the molar concentrations of $Ba^{2+}(aq)$ and $CrO_4^{2-}(aq)$ in the 1.00 L of solution.

New volume = 500. mL + 500. mL = 1.000 L, therefore $[Ba^{2+}]$ in 1.000 L is one-half its initial value: $[Ba^{2+}] = \frac{500.\text{ mL}}{1{,}000.\text{ mL}} \times (8.2 \times 10^{-6}\ M) = 4.1 \times 10^{-6}\ M$ $[CrO_4^{2-}] = \frac{500.\text{ mL}}{1{,}000.\text{ mL}} \times (8.2 \times 10^{-6}\ M) = 4.1 \times 10^{-6}\ M$	One point is earned for the correct concentration.

(ii) Use the molar concentrations of $Ba^{2+}(aq)$ ions and $CrO_4^{2-}(aq)$ ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

The product $Q = [Ba^{2+}][CrO_4^{2-}]$ $= (4.1 \times 10^{-6}\ M)(4.1 \times 10^{-6}\ M)$ $= 1.7 \times 10^{-11}$ Because $Q = 1.7 \times 10^{-11} < 1.2 \times 10^{-10} = K_{sp}$, no precipitate forms.	One point is earned for calculating a value of Q that is consistent with the concentration values in part (d)(i). One point is earned for using Q to explain why no precipitate forms.

1A

1 A i $K_{sp} = [Pb^{2+}][I^-]^2$

ii $[I^-] = 2[Pb^{2+}] = \boxed{0.0026\ M}$

iii $K_{sp} = [x][2x]^2 = 4x^3$

$4x^3 |_{x=1.3\times10^{-3}} = 8.79\times10^{-9} \rightarrow \boxed{8.8\times10^{-9}}$

B $K_{sp} = 8.79\times10^{-9}$

$[Pb^{2+}] = 1.3\times10^{-3}$ $[I^-] = 2.6\times10^{-3}$

The concentrations at equilibrium do not change because the Ksp 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 1 L.

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 $[Ba^{2+}] = \frac{(8.2\times10^{-6})(0.5)}{0.5+0.5} = \boxed{4.1\times10^{-6}\ M}$

$[CrO_4^{2-}] = \frac{(8.2\times10^{-6})(0.5)}{0.5+0.5} = \boxed{4.1\times10^{-6}\ M}$

ii $Q = [Ba^{2+}][CrO_4^{2-}] = (4.1\times10^{-6})^2$

$= 1.681\times10^{-11}$ $1.68\times10^{-11} < 1.2\times10^{-10}$

$Q = 1.681\times10^{-11}$ $K = 1.2\times10^{-10}$ $Q < K$

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.

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1 B

(a) (i) $K_{sp} = [Pb^{+2}][I^-]^2$

(ii) $Pb^{+2} + 2I^-$

Pb^{+2}	$2I^-$
0	0
+x	+2x
$x = 1.3\times10^{-3}$	$2x = 2.6\times10^{-3}$

$\boxed{[I^-] = 2.6\times10^{-3} M}$

(iii) $K_{sp} = [1.3\times10^{-3}][2.6\times10^{-3}]^2$

$\boxed{K_{sp} = 8.8\times10^{-9}}$

(b) $[Pb^{+2}] = 1.3\times10^{-3} M$ and $[I^-] = 2.6\times10^{-3} M$ because that is the largest concentration that can exist in a solution until the solution is supersaturated. $8.8\times10^{-9} = [x][2x]^2 = 4x^3$

$x = 1.3\times10^{-3}$ and $2x = 2.6\times10^{-3}$

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

(d) (i) $M_1V_1 = M_2V_2$ $\quad$ $M_1V_1 = M_2V_2$

$(8.2\times10^{-6})(.5) = (M_2)(1)$ $\quad$ $(8.2\times10^{-6})(.5) = (M_2)(1)$

$[Ba^{+2}] = 4.1\times10^{-6} M$ $\quad$ $[CrO_4^{-2}] = 4.1\times10^{-6} M$

(ii) $K_{sp} \geq [Ba^{+2}][CrO_4^{-2}]$

$1.2\times10^{-10} \geq [4.1\times10^{-6}][4.1\times10^{-6}]$

$1.2\times10^{-10} > 1.7\times10^{-11}$

since K_{sp} is larger than the value of the K_{sp} expression, 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.

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 1 C

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

ii.) $PbI_2 \rightarrow Pb^{2+} + 2I^-$

0 0

-1.3×10^{-3} $+1.3\times10^{-3}$ $+2(1.3\times10^{-3})$

$\boxed{2.6\times10^{-3}\ M = [I^-]}$

b.) Pb^{2+}

$(1.3\times10^{-3}M)(1.0\ L) = 1.3\times10^{-3}$ mol $\frac{1.3\times10^{-3}\ mol}{2\ L} = \boxed{[Pb^{2+}] = 6.5\times10^{-4}\ M}$

I^-

$(2.6\times10^{-3})(1.0L) = 2.6\times10^{-3}$ mol $\frac{2.6\times10^{-3}\ mol}{2\ L} = \boxed{[I^-] = 1.3\times10^{-3}\ M}$

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

d.) $BaCrO_4 \rightarrow Ba^{2+} + CrO_4^{2-}$

i) $8.2\times10^{-6}M$ $8.2\times10^{-6}\ M$

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

$\frac{4.1\times10^{-6}\ mol}{1.0L}$ $\frac{4.1\times10^{-6}\ mol}{1.0L}$

$\boxed{[Ba^{2+}] + [CrO_4^{2-}] = 4.1\times10^{-6}\ M}$

ii) $Q = (4.1\times10^{-6})^2$ $1.7\times10^{-11} < 1.2\times10^{-10}$

$Q = 1.7\times10^{-11}$ $K_{sp} = 1.2\times10^{-10}$ $Q < K$

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}.

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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).