• Calculate the molar solubility of silver sulfide, Ag$_2$S, given that $K_{sp}$ is $8 \times 10^{-51}$ at 25 °C.

The dissolution reaction and solubility product are:

$$\text{Ag}_2\text{S}(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{S}^{2-}(aq) \quad K_{sp} = [\text{Ag}^+(aq)]^2[\text{S}^{2-}(aq)]$$

If $x$ mol of Ag$_2$S dissolve in one litre, then $[\text{Ag}^+(aq)] = 2x$ M and $[\text{S}^{2-}(aq)] = x$ M. Hence:

$$K_{sp} = (2x)^2(x) = 4x^3 = 8 \times 10^{-51} \quad \text{so } x = 1 \times 10^{-17}$$

Answer: $1 \times 10^{-17}$
• Will AgCl precipitate if solutions of 25.0 mL of $2.0 \times 10^{-5}$ M KCl and 75.0 mL of $1 \times 10^{-5}$ M AgNO$_3$ are added to one another? Show your reasoning. 
$K_{sp}$ for AgCl = $1.8 \times 10^{-10}$ at 25 °C.

After mixing the solution has a volume of $(25.0 + 75.0)$ mL = 100.0 mL. Using $c_1V_1 = c_2V_2$, this leads to Ag$^+$ and Cl$^-$ concentrations of:

\[
\begin{align*}
[\text{Ag}^+(\text{aq})] &= (75.0 / 100.0) \times 1 \times 10^{-5} \text{ M} = 7.5 \times 10^{-6} \text{ M} \\
[\text{Cl}^- (\text{aq})] &= (25.0 / 100.0) \times 2.0 \times 10^{-5} \text{ M} = 5 \times 10^{-5} \text{ M}
\end{align*}
\]

AgCl(s) dissolves to give Ag$^+$ (aq) + Cl$^-$ (aq) with the ionic product, $Q_{sp}$:

\[
Q_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^- (\text{aq})] = (7.5 \times 10^{-6}) \times (5 \times 10^{-5}) = 4 \times 10^{-11}
\]

As $Q_{sp} << K_{sp}$, there will be no precipitate.

Answer: No precipitate forms
A saturated solution of lithium carbonate in pure water at 20 °C contains 1.33 g of solute per 100.0 mL of solution. Calculate the aqueous solubility product of lithium carbonate at this temperature.

The molar mass of \( \text{Li}_2\text{CO}_3 \) is \( (2 \times 6.941 \text{ (Li)} + 12.01 \text{ (C)} + 3 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 73.892 \text{ g mol}^{-1} \). A mass of 1.33 g therefore corresponds to:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.33 \text{ g}}{73.892 \text{ g mol}^{-1}} = 0.0180 \text{ mol}
\]

The reaction table for the dissolution of \( \text{Li}_2\text{CO}_3 \) is:

<table>
<thead>
<tr>
<th></th>
<th>( \text{Li}_2\text{CO}_3 )</th>
<th>( \rightleftharpoons )</th>
<th>2( \text{Li}^+ )(aq)</th>
<th>( \text{CO}_3^{2-} )(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0180</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>( -x )</td>
<td></td>
<td>+2( x )</td>
<td>+( x )</td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td>0.0360</td>
<td>0.0180</td>
</tr>
</tbody>
</table>

These number of moles of \( \text{Li}^+ \)(aq) and \( \text{CO}_3^{2-} \)(aq) in 100.0 mL. In a litre, the concentrations are therefore \([\text{Li}^+ \text{ (aq)}] = 0.360 \text{ M} \) and \([\text{CO}_3^{2-} \text{ (aq)}] = 0.180 \text{ M} \). The solubility product is therefore:

\[
K_{sp} = [\text{Li}^+ \text{ (aq)}]^2[\text{CO}_3^{2-} \text{ (aq)}] = (0.360)^2(0.180) = 0.0233
\]

When the temperature of the same solution is raised to 40 °C, the solubility is reduced to 1.17 g per 100.0 mL of solution. What conclusions can be drawn about the sign of the standard enthalpy of dissolution of lithium carbonate?

Increasing the temperature leads to less dissolution: the equilibrium has shifted towards reactants (to the left). According to Le Chatelier’s principle, this is consistent with an exothermic reaction: \( \Delta H < 0 \).
A standard test for the presence of chloride ion in water involves the appearance of a precipitate of AgCl upon addition of 0.05 mL of AgNO₃ (0.03 M) to 100 mL of sample. What is the minimum concentration of Cl⁻ detectable by this method? The $K_{sp}$ of AgCl = $1.8 \times 10^{-10}$.

The number of moles of Ag⁺(aq) in 0.05 mL of a 0.03 M solution of AgNO₃(aq) is:

\[
\text{number of moles} = \text{concentration } \times \text{volume} = (0.03 \text{ mol L}^{-1}) \times (0.05 \times 10^{-3} \text{ L}) = 1.5 \times 10^{-6} \text{ mol}
\]

When this is added to 100. mL of the sample:

\[
[\text{Ag}^+(aq)] = \frac{\text{number of moles}}{\text{volume}} = (1.5 \times 10^{-6} \text{ mol}) / (0.100 \text{ L}) = 1.5 \times 10^{-5} \text{ M}
\]

For AgCl(s), $K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)]$ and so:

\[
[\text{Cl}^-(aq)] = \frac{K_{sp}}{[\text{Ag}^+(aq)]} = \frac{1.8 \times 10^{-10}}{1.5 \times 10^{-5}} = 1.2 \times 10^{-5}
\]

Answer: $1.2 \times 10^{-5}$
What is the molar solubility of \( \text{Cu(OH)}_2 \) at 25 °C given its \( K_{sp} = 4.5 \times 10^{-21} \text{M}^3 \)?

The solubility expression and product for \( \text{Cu(OH)}_2(\text{s}) \) are:

\[
\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \quad K_{sp} = [\text{Cu}^{2+}(\text{aq})][\text{OH}^-(\text{aq})]^2
\]

If the molar solubility is \( S \), \([\text{Cu}^{2+}(\text{aq})] = S \) and \([\text{OH}^- (\text{aq})] = 2S \). Hence,

\[
K_{sp} = (S) \times (2S)^2 = 4S^3 = 4.5 \times 10^{-21}
\]

\[
S = 1.0 \times 10^{-7} \text{M}
\]

Answer: \( 1.0 \times 10^{-7} \text{M} \)
The molar solubility of lead(II) fluoride, PbF₂, is found to be \(2.6 \times 10^{-3}\) M at 25 °C. Calculate the value of \(K_{sp}\) for this compound at this temperature.

The solubility equilibrium and constant for PbF₂(s) are,

\[\text{PbF}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{F}^-(aq) \quad K_{sp} = [\text{Pb}^{2+}(aq)][\text{F}^-(aq)]^2\]

As one moles of Pb²⁺(aq) and two moles of F⁻(aq) are produced for every mole of PbF₂(s) which dissolves, [Pb²⁺(aq)] = \(2.6 \times 10^{-3}\) M and [F⁻(aq)] = \((2 \times 2.6 \times 10^{-3}) = 5.2 \times 10^{-3}\) M. Hence,

\[K_{sp} = (2.6 \times 10^{-3}) \times (5.2 \times 10^{-3})^2 = 7.0 \times 10^{-8}\]

\[K_{sp} = 7.0 \times 10^{-8}\]
The active ingredient in aspirin is the monoprotic acid, acetylsalicylic acid (HC$_9$H$_7$O$_4$) that has a $K_a$ of $3.3 \times 10^{-4}$ M at 25 °C. What is the pH of a solution obtained when a tablet containing 200 mg of acetylsalicylic acid is dissolved in 125 mL of water?

The molar mass is $(8\times1.008 \text{ (H)}) + (9\times12.01 \text{ (O)}) \text{ g mol}^{-1} = 180.154 \text{ g mol}^{-1}$ so 200 mg contains:

$$n(\text{HC}_9\text{H}_7\text{O}_4) = \frac{\text{mass}}{\text{molar mass}} = \frac{200 \times 10^{-3} \text{ g}}{180.154 \text{ g mol}^{-1}} = 1.11 \times 10^{-3} \text{ mol}$$

When this amount is dissolved in 125 mL, the concentration is:

$$n[\text{HC}_9\text{H}_7\text{O}_4] = \frac{\text{number of moles}}{\text{volume}} = \frac{1.11 \times 10^{-3} \text{ mol}}{(125/1000) \text{ L}} = 8.88 \times 10^{-3} \text{ M}$$

The reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>HC$_9$H$_7$O$_4$</th>
<th>H$_2$O</th>
<th>$\rightleftharpoons$</th>
<th>H$_3$O$^+$</th>
<th>C$_9$H$_7$O$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>$8.88\times10^{-3}$</td>
<td>large</td>
<td>$0$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>$-x$</td>
<td>negligible</td>
<td>$+x$</td>
<td>$+x$</td>
<td>$x$</td>
</tr>
<tr>
<td>final</td>
<td>$8.88\times10^{-3} - x$</td>
<td>large</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{C}_9\text{H}_7\text{O}_4^-(aq)]}{[\text{HC}_9\text{H}_7\text{O}_4(aq)]} = \frac{x^2}{(8.88\times10^{-3} - x)} = 3.3 \times 10^{-4}$$

$K_a$ is not sufficiently small in comparison to the initial concentration of acid that any approximation to this equation can be made. Hence, the quadratic expression must be solved:

$$x^2 = (3.3\times10^{-4} \times 8.88\times10^{-3}) - (3.3\times10^{-4})x$$

$$x^2 + (3.3\times10^{-4})x - (2.9\times10^{-6})$$

With $a = 1$, $b = +3.3\times10^{-4}$ and $c = -2.9\times10^{-6}$, the roots are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-3.3 \times 10^{-4} \pm \sqrt{(3.3 \times 10^{-4})^2 - (4 \times 1 \times -2.9 \times 10^{-6})}}{2 \times 1}$$

Only the positive root has physical significance so $x = 1.55 \times 10^{-3}$

$$[\text{H}_3\text{O}^+(aq)] = x = 1.55\times10^{-3} \text{ M}, \text{ pH} = -\log_{10}([\text{H}_3\text{O}^+(aq)]) = -\log_{10}(1.55 \times 10^{-3}) = 2.81$$

Answer: pH = 2.81
A standard test for the presence of chloride ion in water involves the appearance of a precipitate of AgCl upon addition of 1 mL of AgNO₃ (0.03 M) to 100 mL of the water sample. What is the minimum concentration of Cl⁻ detectable by this method? 

\[ K_{sp}(AgCl) = 1.8 \times 10^{-10} \text{ M}^2 \]

The number of moles of Ag⁺(aq) in 1 mL of 0.03 M AgNO₃ is:

\[ n(\text{Ag}^+ (\text{aq})) = \text{concentration} \times \text{volume} = (0.03 \text{ M}) \times (1 \times 10^{-3} \text{ L}) = 3 \times 10^{-5} \text{ mol} \]

In the test, this amount is present in (100 + 1) = 101 mL so its concentration is:

\[ [\text{Ag}^+ (\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{(3\times10^5 \text{ mol})}{(101\times10^{-3} \text{ L})} = 3 \times 10^{-4} \text{ M} \]

The solubility equilibrium and product for AgCl are given by:

\[ \text{AgCl(s)} \leftrightharpoons \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \]

\[ K_{sp} = [\text{Ag}^+ (\text{aq})][\text{Cl}^- (\text{aq})] = 1.8 \times 10^{-10} \]

Hence,

\[ [\text{Cl}^- (\text{aq})] = \frac{K_{sp}}{[\text{Ag}^+ (\text{aq})]} = \frac{(1.8 \times 10^{-10})}{(3 \times 10^{-4})} = 6 \times 10^{-7} \text{ M} \]

If [Cl⁻(aq)] is less than this value, AgCl will not precipitate.

Answer: [Cl⁻(aq)] = 6 \times 10^{-7} \text{ M}
Uric acid, \( \text{C}_5\text{H}_5\text{N}_4\text{O}_3 \), is a weak diprotic acid with a low solubility of 70 mg L\(^{-1}\). The extremely painful inflammation known as gout occurs when crystals of uric acid are deposited in the joints. Given that the pH of a saturated solution of uric acid is 4.58, calculate the \( pK_{a1} \) of uric acid at 25 °C?

As \( \text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})] \) 4.58, \([\text{H}_3\text{O}^+(\text{aq})] = 10^{4.58} = 2.63 \times 10^{-5} \) M.

The molar mass of uric acid is:

\[
(5 \times 12.01 \text{ (C)}) + (5 \times 1.008 \text{ (H)}) + (4 \times 14.01 \text{ (N)}) + (3 \times 16.00 \text{ (O)}) = 169.13 \text{ g mol}^{-1}
\]

A one litre solution contains 70 mg corresponding to

number of moles = \( \frac{(70 \times 10^{-3} \text{ g})}{(169.13 \text{ g mol}^{-1})} = 4.1 \times 10^{-4} \text{ mol} \).

For this weak acid, the reaction table is:

<table>
<thead>
<tr>
<th>( \text{C}_5\text{H}_5\text{N}_4\text{O}_3 )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \rightleftharpoons )</th>
<th>( \text{H}_3\text{O}^+ )</th>
<th>( \text{C}_5\text{H}_5\text{N}_4\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>( 4.1 \times 10^{-4} )</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>final</td>
<td>( (4.1 \times 10^{-4}) - (2.63 \times 10^{-5}) )</td>
<td>large</td>
<td>( 2.63 \times 10^{-5} )</td>
<td>( 2.63 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

The equilibrium constant \( K_{a1} \) is given by:

\[
K_{a1} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_5\text{H}_5\text{N}_4\text{O}_3^- (\text{aq})]}{[\text{C}_5\text{H}_5\text{N}_4\text{O}_3 (\text{aq})]} = \frac{(2.63 \times 10^{-5}) \times (2.63 \times 10^{-5})}{(3.9 \times 10^{-4})} = 1.8 \times 10^6
\]

Hence, \( pK_{a1} = -\log_{10}(1.8 \times 10^6) = 5.7 \)

Answer: \( pK_{a1} = 5.7 \)

The monosodium salt of uric acid is slightly more soluble, \( 8 \times 10^{-4} \) g mL\(^{-1}\). Calculate the solubility product constant, \( K_{sp} \), of sodium urate at 25 °C. Assume no hydrolysis of the urate ion occurs.

The formula mass of the monosodium salt, \( \text{NaC}_5\text{H}_5\text{N}_4\text{O}_3 \) is 22.99 (Na) + \((5 \times 12.01 \text{ (C)}) + (4 \times 1.008 \text{ (H)}) + (4 \times 14.01 \text{ (N)}) + (3 \times 16.00 \text{ (O)}) = 191.112. \) The molar solubility is:

\[
\text{molar solubility} = \frac{\text{solubility}}{\text{formula mass}} = \frac{(8 \times 10^{-4} \text{ g mL}^{-1})}{(191.112 \text{ g mol}^{-1})}
= 4 \times 10^{-6} \text{ mol mL}^{-1} = 4 \times 10^{-3} \text{ M}
\]

Hence, \( K_{sp} = [\text{Na}^+(\text{aq})][\text{C}_5\text{H}_5\text{N}_4\text{O}_3^- (\text{aq})] = (4 \times 10^{-3}) \times (4 \times 10^{-3}) = 2 \times 10^{-5} \)

Answer: \( K_{sp} = 2 \times 10^{-5} \)
Suggest a possible reason why the pH of blood plasma remains near 7.4 even when saturated with uric acid.

**Blood is buffered by a CO$_3^{2-}$ / HCO$_3^{-}$ buffering system which resists changes in pH.**