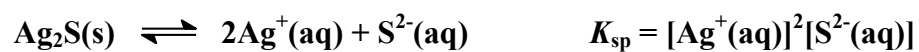


Marks
3

- Calculate the molar solubility of silver sulfide, Ag_2S , given that K_{sp} is 8×10^{-51} at 25°C .

The dissolution reaction and solubility product are:



**If x mol of Ag_2S dissolve in one litre, then $[\text{Ag}^+(\text{aq})] = 2x \text{ M}$ and $[\text{S}^{2-}(\text{aq})] = x \text{ M}$.
Hence:**

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

Answer: 1×10^{-17}

<ul style="list-style-type: none">Will AgCl precipitate if solutions of 25.0 mL of 2.0×10^{-5} M KCl and 75.0 mL of 1×10^{-5} M AgNO₃ are added to one another? Show your reasoning. K_{sp} for AgCl = 1.8×10^{-10} at 25 °C.	Marks 2
<p>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:</p> $[\text{Ag}^+(\text{aq})] = (75.0 / 100.0) \times 1 \times 10^{-5} \text{ M} = 7.5 \times 10^{-6} \text{ M}$ $[\text{Cl}^-(\text{aq})] = (25.0 / 100.0) \times 2.0 \times 10^{-5} \text{ M} = 5 \times 10^{-5} \text{ M}$ <p>AgCl(s) dissolves to give Ag⁺(aq) + Cl⁻(aq) with the ionic product, Q_{sp}:</p> $Q_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] = (7.5 \times 10^{-6}) \times (5 \times 10^{-5}) = 4 \times 10^{-11}$ <p>As $Q_{sp} \ll K_{sp}$, there will be no precipitate.</p>	
	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 Li_2CO_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 Li_2CO_3 is:

	Li_2CO_3	\rightleftharpoons	$2\text{Li}^+(\text{aq})$	$\text{CO}_3^{2-}(\text{aq})$
Initial	0.0180		0	0
Change	-x		+2x	+x
Equilibrium	-		0.0360	0.0180

These number of moles of $\text{Li}^+(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$ 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:

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

$$K_{\text{sp}} = 0.0233$$

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 = 1.8×10^{-10} .

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

$$\begin{aligned}\text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.03 \text{ mol L}^{-1}) \times (0.05 \times 10^{-3} \text{ L}) = 1.5 \times 10^{-6} \text{ mol}\end{aligned}$$

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

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

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

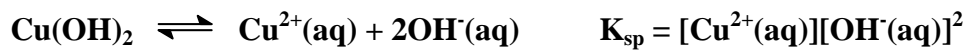
$$[\text{Cl}^-(\text{aq})] = K_{sp} / [\text{Ag}^+(\text{aq})] = 1.8 \times 10^{-10} / 1.5 \times 10^{-5} = 1.2 \times 10^{-5}$$

Answer: 1.2×10^{-5}

Marks
2

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

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



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

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

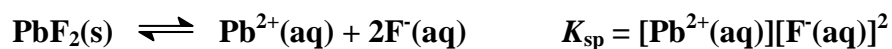
$$\text{S} = 1.0 \times 10^{-7} \text{ M}$$

Answer: $1.0 \times 10^{-7} \text{ M}$

Marks
2

- The molar solubility of lead(II) fluoride, PbF_2 , is found to be $2.6 \times 10^{-3} \text{ M}$ at 25°C . Calculate the value of K_{sp} for this compound at this temperature.

The solubility equilibrium and constant for $\text{PbF}_2(\text{s})$ are,



As one moles of $\text{Pb}^{2+}(\text{aq})$ and two moles of $\text{F}^{-}(\text{aq})$ are produced for every mole of $\text{PbF}_2(\text{s})$ which dissolves, $[\text{Pb}^{2+}(\text{aq})] = 2.6 \times 10^{-3} \text{ M}$ and $[\text{F}^{-}(\text{aq})] = (2 \times 2.6 \times 10^{-3}) = 5.2 \times 10^{-3} \text{ M}$. Hence,

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

$$K_{\text{sp}} = 7.0 \times 10^{-8}$$

Marks
3

- The active ingredient in aspirin is the monoprotic acid, acetylsalicylic acid ($\text{HC}_9\text{H}_7\text{O}_4$) that has a K_a of 3.3×10^{-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 $(8 \times 1.008 (\text{H})) + (9 \times 12.01) + (4 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 180.154 \text{ g mol}^{-1}$ 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:

	$\text{HC}_9\text{H}_7\text{O}_4$	H_2O	\rightleftharpoons	H_3O^+	$\text{C}_9\text{H}_7\text{O}_4^-$
initial	8.88×10^{-3}	large		0	0
change	$-x$	negligible		$+x$	$+x$
final	$8.88 \times 10^{-3} - x$	large		x	x

The equilibrium constant K_a is given by:

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

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:

$$x^2 = (3.3 \times 10^{-4} \times 8.88 \times 10^{-3}) - (3.3 \times 10^{-4})x$$

$$x^2 + (3.3 \times 10^{-4})x - (2.9 \times 10^{-6})$$

With $a = 1$, $b = +3.3 \times 10^{-4}$ and $c = -2.9 \times 10^{-6}$, 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 $x = 1.55 \times 10^{-3}$

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

Answer: pH = 2.81

ANSWER CONTIUNES ON THE NEXT PAGE

- 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? $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10} \text{ M}^2$.

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:

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

The solubility equilibrium and product for AgCl are given by:



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

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.

$$\text{Answer: } [\text{Cl}^-(\text{aq})] = 6 \times 10^{-7} \text{ M}$$

Marks
7

- Uric acid, $C_5H_5N_4O_3$, 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, $[\text{H}_3\text{O}^+(\text{aq})] = 10^{4.58} = 2.63 \times 10^{-5} \text{ M}$.

The molar mass of uric acid is:

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

A one litre solution contains 70 mg corresponding to

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

For this weak acid, the reaction table is:

	$C_5H_5N_4O_3$	H_2O	\rightleftharpoons	H_3O^+	$C_5H_4N_4O_3^-$
initial	4.1×10^{-4}	large		0	0
final	$(4.1 \times 10^{-4}) - (2.63 \times 10^{-5})$	large		2.63×10^{-5}	2.63×10^{-5}

The equilibrium constant K_{a1} is given by:

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

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

Answer: $pK_{a1} = 5.7$

The monosodium salt of uric acid is slightly more soluble, $8 \times 10^{-4} \text{ g mL}^{-1}$. 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, $\text{NaC}_5\text{H}_4\text{N}_4\text{O}_3$ is $22.99 (\text{Na}) + (5 \times 12.01 (\text{C})) + (4 \times 1.008 (\text{H})) + (4 \times 14.01 (\text{N})) + (3 \times 16.00 (\text{O})) = 191.112$. 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, $K_{sp} = [\text{Na}^+(\text{aq})][\text{C}_5\text{H}_4\text{N}_4\text{O}_3^-(\text{aq})] = (4 \times 10^{-3}) \times (4 \times 10^{-3}) = 2 \times 10^{-5}$

Answer: $K_{sp} = 2 \times 10^{-5}$

ANSWER CONTIUNES ON THE NEXT PAGE

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 $\text{CO}_3^{2-} / \text{HCO}_3^-$ buffering system which resists changes in pH.