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:

$$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq) \qquad K_{sp} = [Ag^+(aq)]^2[S^{2-}(aq)]$$

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

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

Answer: **1×10^{-17}**

Marks
2

- 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 $AgNO_3$ are added to one another? Show your reasoning. K_{sp} for AgCl = 1.8×10^{-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:

$[Ag^+(aq)] = (75.0 / 100.0) \times 1 \times 10^{-5}$ M = 7.5×10^{-6} M

$[Cl^-(aq)] = (25.0 / 100.0) \times 2.0 \times 10^{-5}$ M = 5×10^{-5} M

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

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

As $Q_{sp} \ll K_{sp}$, 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. **4**

The molar mass of Li_2CO_3 is (2 × 6.941 (Li) + 12.01 (C) + 3 × 16.00 (O)) g mol^{-1} = 73.892 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	$\rightleftharpoons$	$2Li^+(aq)$	$CO_3^{2-}(aq)$
Initial	**0.0180**		**0**	**0**
Change	**-*x***		**+2*x***	**+*x***
Equilibrium	**-**		**0.0360**	**0.0180**

These number of moles of $Li^+(aq)$ and $CO_3^{2-}(aq)$ in 100.0 mL. In a litre, the concentrations are therefore $[Li^+(aq)]$ = 0.360 M and $[CO_3^{2-}(aq)]$ = 0.180 M. The solubility product is therefore:

$$K_{sp} = [Li^+(aq)]^2[CO_3^{2-}(aq)] = (0.360)^2(0.180) = 0.0233$$

K_{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: Δ*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 $AgNO_3$ (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}. **3**

The number of moles of Ag^+(aq) in 0.05 mL of a 0.03 M solution of $AgNO_3$(aq) is:

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

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

$[Ag^+(aq)]$ = number of moles / volume
= (`1.5×10^{-6} mol) / (0.100 L) = 1.5×10^{-5} M

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

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

Answer: **1.2×10^{-5}**

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

Marks 2

The solubility expression and product for $Cu(OH)_2(s)$ are:

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

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

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

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

Answer: **1.0×10^{-7} M**

Marks
2

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

The solubility equilibrium and constant for PbF_2(s) are,

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Pb^{2+}(aq)][F^-(aq)]^2$$

As one moles of Pb^{2+}(aq) and two moles of F^-(aq) are produced for every mole of PbF_2(s) which dissolves, $[Pb^{2+}(aq)] = 2.6 \times 10^{-3}$ 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 × 10^{-8}**

Marks 3

- The active ingredient in aspirin is the monoprotic acid, acetylsalicylic acid ($HC_9H_7O_4$) 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 (8×1.008 (H)) + (9×12.01) + (4×16.00 (O)) g mol^{-1} = 180.154 g mol^{1} so 200 mg contains:

$$n(HC_9H_7O_4) = \frac{\text{mass}}{\text{molar mass}} = \frac{(200 \times 10^{-3}\text{ g})}{(180.154\text{ g mol}^{-1})} = 1.11 \times 10^{-3}\text{ mol}$$

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

$$n[HC_9H_7O_4] = \frac{\text{number of moles}}{\text{volume}} = \frac{(1.11 \times 10^{-3}\text{ mol})}{(125/1000\text{ L})} = 8.88 \times 10^{-3}\text{ M}$$

The reaction table is:

	$HC_9H_7O_4$	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	8.88×10^{-3}	large		0	0
change	$-x$	negligible		$+x$	$+x$
final	$8.88\times10^{-3} - x$	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+(aq)][C_9H_7O_4^-(aq)]}{[HC_9H_7O_4(aq)]} = \frac{x^2}{(8.88 \times 10^{-3} - x)} = 3.3 \times 10^{-4}$$

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:

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

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

With a = 1, b = +3.3×10^{-4} and c = -2.9×10^{-6}, the roots are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(3.3 \times 10^{-4}) \pm \sqrt{(3.3 \times 10^{-4})^2 - (4 \times 1 \times -2.9 \times 10^{-5})}}{(2 \times 1)}$$

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

$[H_3O^+(aq)] = x = 1.55\times10^{-3}$ M, pH = $-\log_{10}([H_3O^+(aq)]) = -\log_{10}(1.55 \times 10^{-3}) = 2.81$

Answer: **pH = 2.81**

ANSWER CONTIUNES ON THE NEXT PAGE

2

- 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 $AgNO_3$ (0.03 M) to 100 mL of the water sample. What is the minimum concentration of Cl^- detectable by this method? K_{sp} (AgCl) = 1.8×10^{-10} M^2.

The number of moles of Ag^+(aq) in 1 mL of 0.03 M $AgNO_3$ is:

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

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

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

The solubility equilibrium and product for AgCl are given by:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

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

Hence,

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

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

Answer: $[Cl^-(aq)] = = 6 \times 10^{-7}$ 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 pH = $-\log_{10}([H_3O^+(aq)])$ 4.58, $[H_3O^+(aq)] = 10^{4.58} = 2.63 \times 10^{-5}$ M.

The molar mass of uric acid is:

((5×12.01 (C)) + (5×1.008 (H)) + (4×14.01 (N)) + (3×16.00 (O)) g mol^{-1} = 169.13 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	$(4.1\times10^{-4}) - (2.63 \times 10^{-5})$	large		2.63×10^{-5}	2.63×10^{-5}

The equilibrium constant K_{a1} is given by:

$$K_{a1} = \frac{[H_3O^+(aq)][C_5H_4N_4O_3^-(aq)]}{[C_5H_5N_4O_3(aq)]} = \frac{(2.63\times10^{-5})\times(2.63\times10^{-5})}{(3.9\times10^{-4})} = 1.8 \times 10^{-6}$$

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, 8×10^{-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, $NaC_5H_4N_4O_3$ is 22.99 (Na) + (5×12.01 (C)) + (4×1.008 (H)) + (4×14.01 (N)) + (3×16.00 (O)) = 191.112. The molar solubility is:

$$\text{molar solubility} = \frac{\text{solubility}}{\text{formula mass}} = \frac{(8\times10^{-4}\ \text{g mL}^{-1})}{(191.112\ \text{g mol}^{-1})}$$
$$= = 4\times10^{-6}\ \text{mol mL}^{-1} = 4\times10^{-3}\ \text{M}$$

Hence, $K_{sp} = [Na^+(aq)][C_5H_4N_4O_3^-(aq)] = (4 \times 10^{-3}) \times (4 \times 10^{-3}) = 2 \times 10^{-5}$

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 CO_3^{2-} / HCO_3^{-} buffering system which resists changes in pH.