Tutorial 16: Solubility Equilibria - Answers to Practice Questions

4 **(a)** **(i)** Let the solubility of PbI_2 in pure water be s mol dm^{-3}.

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

At equilibrium in the saturated solution, $[Pb^{2+}] = s$ mol dm^{-3}
$[I^-] = 2s$ mol dm^{-3}

$$K_{sp} = \left[Pb^{2+}\right]\left[I^-\right]^2$$
$$7.1\times10^{-9} = (s)(2s)^2$$
$$4s^3 = 7.1\times10^{-9}$$
$$s = \left(\frac{7.1\times10^{-9}}{4}\right)^{1/3} = 1.21\times10^{-3} \text{ mol dm}^{-3}$$

Hence solubility of PbI_2 in pure water = <u>1.21 x 10^{-3} mol dm^{-3}</u>

(ii) Let the solubility of PbI_2 in 0.10 mol dm^{-3} BaI_2 solution be y mol dm^{-3}.

$$BaI_2(aq) \rightarrow Ba^{2+}(aq) + 2I^-(aq)$$
$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

At equilibrium in the saturated solution, $[Pb^{2+}] = y$ mol dm^{-3}
$[I^-] = 2y + (2)(0.10)$
$= (2y + 0.20)$ mol dm^{-3}

$$K_{sp} = \left[Pb^{2+}\right]\left[I^-\right]^2 = (y)(2y + 0.20)^2 = 7.1\times10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

Since PbI_2 is sparingly soluble in water and the presence of I^- ions from BaI_2 further suppresses its solubility, $2y << 0.20$. Thus, $(2y + 0.20) \approx 0.20$.

$$(y)(0.20)^2 = 7.1\times10^{-9}$$
$$y = \left(\frac{7.1\times10^{-9}}{(0.20)^2}\right) = 1.78\times10^{-7} \text{ mol dm}^{-3}$$

Hence solubility of PbI_2 in 0.10 mol dm^{-3} BaI_2 solution = <u>1.78 x 10^{-7} mol dm^{-3}</u>

(iii) Let the solubility of PbI_2 in 0.20 mol dm^{-3} $Pb(NO_3)_2$ solution be w mol dm^{-3}.

$$Pb(NO_3)_2(aq) \rightarrow Pb^{2+}(aq) + 2NO_3^-(aq)$$
$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

At equilibrium in the saturated solution, $[Pb^{2+}] = (w + 0.20)$ mol dm^{-3}
$[I^-] = 2w$ mol dm^{-3}

$$K_{sp} = \left[Pb^{2+}\right]\left[I^-\right]^2 = (w + 0.20)(2w)^2 = 7.1\times10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

Since PbI_2 is sparingly soluble in water and the presence of Pb^{2+} ions from $Pb(NO_3)_2$ further suppresses its solubility, w << 0.20. Thus, (w + 0.20) ≈ 0.20.

$$(0.20)(2w)^2 = 7.1\times10^{-9}$$

$$w = \sqrt{\frac{7.1\times10^{-9}}{(0.20)(2)^2}} = 9.42\times10^{-5} \text{ mol dm}^{-3}$$

∴ solubility of PbI_2 in 0.20 mol dm^{-3} $Pb(NO_3)_2$ solution = <u>9.42 x 10^{-5} mol dm^{-3}</u>

(b) (i) Let [KI] be x mol dm^{-3}.

$$KI(aq) \rightarrow K^+(aq) + I^-(aq)$$
$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

At equilibrium in the saturated solution, $[Pb^{2+}]$ = 1.0 x 10^{-4} mol dm^{-3}
$[I^-]$ = (2.0 x 10^{-4} + x) mol dm^{-3}

$$K_{sp} = \left[Pb^{2+}\right]\left[I^-\right]^2$$
$$7.1\times10^{-9} = (1.0\times10^{-4})(2.0\times10^{-4} + x)^2$$
$$x = \sqrt{\frac{7.1\times10^{-9}}{1.0\times10^{-4}}} - 2.0\times10^{-4} = 8.23\times10^{-3} \text{ mol dm}^{-3}$$

Hence [KI] = <u>8.23 x 10^{-3} mol dm^{-3}</u>

(ii) When PbI_2 is shaken with water, the following equilibrium is established:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \text{ -----(1)}$$

When a large excess of KI is added and the mixture shaken, the Pb^{2+} ions react with I^- to form the <u>soluble complex, $[PbI_4]^{2-}$</u>, as shown below.

$$Pb^{2+}(aq) + 4I^-(aq) \rightleftharpoons [PbI_4]^{2-}(aq) \text{ -----(2)}$$

The formation of $[PbI_4]^{2-}$ <u>decreases</u> the uncomplexed <u>$[Pb^{2+}]$</u> in the solution.

To counteract the decrease in $[Pb^{2+}]$, the <u>equilibrium position of reaction (1) shifts to the right</u>, resulting in more PbI_2 dissolving and the solubility of PbI_2 is increased.

When sufficient KI is added, the <u>ionic product, $[Pb^{2+}][I^-]^2$, will be less than K_{sp}</u> and hence all the PbI_2 dissolves.

5 **(a)** When ZnF_2 is shaken with water and the undissolved ZnF_2 filtered off, a saturated solution of ZnF_2 is produced.

Let solubility of ZnF_2 be s mol dm^{-3}.
$[Zn^{2+}]$ = s mol dm^{-3}
$[F^-]$ = 2s mol dm^{-3}

$K_{sp} = [Zn^{2+}][F^-]^2 = (s)(2s)^2 = 4s^3 = 3.2 \times 10^{-2}$ mol^3 dm^{-9}
s = 0.2 mol dm^{-3}
$[F^-]$ = 2s = <u>0.400 mol dm^{-3}</u>

(b) When BaF_2 just precipitates, $[F^-]$ = 0.4 mol dm^{-3}.

K_{sp} of BaF_2 = Ionic product of BaF_2
$1.6 \times 10^{-7} = [Ba^{2+}][F^-]^2$
$= [Ba^{2+}](0.4)^2$
$[Ba^{2+}]$ = <u>1.00×10^{-6} mol dm^{-3}</u>

6 **(a)** In the resultant solution before adding solid KF,
$[Ca^{2+}] = (½)(0.100) = 0.0500$ mol dm^{-3}
$[Ba^{2+}] = (½)(0.100) = 0.0500$ mol dm^{-3}

**concentration is halved as volume is doubled when the two solution are mixed together.*

To ppt out max. amount of CaF_2 with no BaF_2 ppt,
ionic product of BaF_2 cannot be greater than K_{sp} of BaF_2,
i.e. $[F^-]$ in the solution is just high enough to make the ionic product of BaF_2 = K_{sp} of BaF_2.

$$K_{sp} = \left[Ba^{2+}\right]\left[F^-\right]^2$$
$$\left[F^-\right] = \sqrt{\frac{K_{sp}}{\left[Ba^{2+}\right]}} = \sqrt{\frac{1.84 \times 10^{-7}}{0.0500}} = \underline{1.92 \times 10^{-3} \text{ mol dm}^{-3}}$$

(b) K_{sp} of $CaF_2 = [Ca^{2+}][F^-]^2$

When $[F^-] = 1.918 \times 10^{-3}$ mol dm^{-3},
$$K_{sp} = \left[Ca^{2+}\right]\left[F^-\right]^2$$
$$\left[Ca^{2+}\right] = \frac{K_{sp}}{\left[F^-\right]^2} = \frac{3.45 \times 10^{-11}}{(1.918 \times 10^{-3})^2} = \underline{9.38 \times 10^{-6} \text{ mol dm}^{-3}}$$

(c) Percentage of Ca^{2+} remaining in solution = $\frac{9.38 \times 10^{-6}}{0.05} \times 100\% = 0.0188\%$

The separation was very <u>effective</u> as <u>almost 100% of the Ca^{2+} has been removed</u> from solution.

7 **(a)** K_{sp} of $Ca(OH)_2 = [Ca^{2+}][OH^-]^2$

(b) **(i)** $OH^-(aq) + HCl(aq) \rightarrow H_2O(l) + Cl^-(aq)$

Amount of OH^- in 25.0 cm^3 filtrate

$= \text{Amount of HCl used} = \frac{20.0}{1000} \times 0.050 = 1.00 \times 10^{-3} \text{ mol}$

$[OH^-] \text{ in the filtrate} = \frac{1.00 \times 10^{-3}}{25.0} \times 1000 = \underline{0.0400 \text{ mol dm}^{-3}}$

(ii) Let the solubility of $Ca(OH)_2$ in 0.010 mol dm^{-3} NaOH be y mol dm^{-3}.

Concentration/mol dm^{-3}	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	
Initial	-	0.010
Change	+y	+2y
Equilibrium	y	(0.010 + 2y)

$\Rightarrow$ Using $[OH^-]$ from (b)(i),

$0.010 + 2y = 0.0400$

$y = 0.0150$

K_{sp} of $Ca(OH)_2 = [Ca^{2+}][OH^-]^2 = (y)(0.010 + 2y)^2$

$= (0.0150)(0.0400)^2$

$= \underline{2.40 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}}$

(c) Let the [NaOH] be y mol dm^{-3}.

Upon mixing the two solutions and assuming no reaction,

$[NaOH] = \frac{y}{2} \text{ mol dm}^{-3}$

$[Ca(OH)_2] = \frac{0.010}{2} = 0.0050 \text{ mol dm}^{-3}$

**concentration is halved as volume is doubled when the two solution are mixed together.*

Hence in the resultant solution,

$[Ca^{2+}] = 0.0050 \text{ mol dm}^{-3}$

$[OH^-] = \left(\frac{y}{2} + 2 \times 0.0050\right) = \left(\frac{y}{2} + 0.010\right) \text{mol dm}^{-3}$

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

For precipitation to takes place, solution must first be saturated with respect to $Ca(OH)_2$, i.e. ionic product of $Ca(OH)_2$ = K_{sp} of $Ca(OH)_2$

$$[Ca^{2+}][OH^-]^2 = 2.40 \times 10^{-5}$$

$$(0.0050)\left(\frac{y}{2} + 0.010\right)^2 = 2.40 \times 10^{-5}$$

$$y = 0.119$$

Hence [NaOH(aq)] = <u>0.119 mol dm^{-3}</u>.

(d) <u>No effect on K_{sp}</u> as <u>temperature is kept constant</u> at 25 °C (K_{sp} only changes with temperature).

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ ----- (1)

When solid $Ca(NO_3)_2$ is added, the <u>Ca^{2+}</u> ions from $Ca(NO_3)_2$ exerts a **<u>common ion effect</u>** and causes the equilibrium position of (1) to shift <u>left</u>, <u>reducing the solubility of $Ca(OH)_2$</u> in water.

(e) **(i)** At 25 °C, pOH = 14 – 12.3 = 1.7
[OH^-] at 25 °C = $10^{-1.7}$ = <u>2.00 x 10^{-2} mol dm^{-3}</u>

At 32 °C, K_w = 1.70 x 10^{-14} mol^2 dm^{-6} $\Rightarrow$ pK_w = –lg K_w = 13.77
pOH at 32 °C = 13.77 – 11.7 = 2.07
[OH^-] at 32 °C = $10^{-2.07}$ = <u>8.51 x 10^{-3} mol dm^{-3}</u>

Alternative workings to calculate [OH^-] at 32°C (simpler):

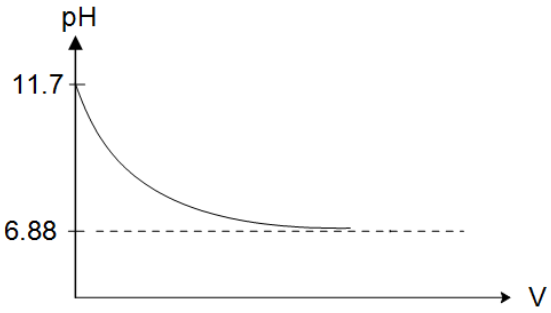
[OH^-] at 32 °C = $\frac{K_W}{[H^+]} = \frac{1.70 \times 10^{-14}}{10^{-11.7}}$ = <u>8.52 x 10^{-3} mol dm^{-3}</u>

At a <u>higher temperature</u>, <u>[OH^-] decreases</u>. Hence, there must be <u>lesser extent of dissolution</u> of $Ca(OH)_2(s)$ at a higher temperature.

According to Le Chatelier's Principle, an increase in temperature will favour the endothermic reaction. Therefore, the <u>dissolution of $Ca(OH)_2$ is exothermic</u>.

(ii) K_{sp} <u>decreases</u> (from **(e)(i)**, when temperature increases, there is lesser extent of dissolution of $Ca(OH)_2(s)$, i.e. solubility decreases).

(iii)



At infinite dilution, the pH of the solution approaches that of pure water at the same temperature such that [H^+] ≈ [OH^-].

$K_w = [H^+][OH^-] = 1.70 \times 10^{-14}$ mol^2 dm^{-6} (at 32 °C)

$[H^+] = \sqrt{1.70 \times 10^{-14}} = 1.304 \times 10^{-7}$ mol dm^{-3}

pH = –lg (1.304×10^{-7}) = 6.88

(f) Add to soil to reduce acidity in soil.
(https://www.chemguide.uk/14to16/largescale/limestone.html)

8 **(a)** When $BaCO_3(s)$ and $BaSO_4(s)$ are added separately to water to form saturated solutions, the following equilibria are established.

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq) \text{ .....(1)}$$

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \text{ .....(2)}$$

When HC*l*(aq) is added, an acid-base reaction takes place, causing the $[CO_3^{2-}]$ to decrease.

$$2H^+ + CO_3^{2-} \longrightarrow CO_2 + H_2O$$

To counteract the decrease in $[CO_3^{2-}]$, the equilibrium position of reaction (1) shifts right, resulting in the dissolution of $BaCO_3$.

With sufficient HC*l*(aq) added, the ionic product, $[Ba^{2+}][CO_3^{2-}]$, will be less than K_{sp} and hence all the $BaCO_3$ eventually dissolves to form a colourless solution.

On the other hand, HC*l*(aq) (or H^+) does not react with SO_4^{2-}. Ignoring dilution effects, the equilibrium position of reaction (2) does not shift and $BaSO_4$ does not dissolve.

(b) $NH_3(aq)$ is a weak base that undergoes partial ionisation in water to produce OH^- ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \text{ ----- (1)}$$

When $NH_3(aq)$ is added to MgC*l*$_2$(aq), the $[OH^-]$ in the solution is increased. At that instant, the ionic product, $[Mg^{2+}][OH^-]^2$, exceeds the K_{sp} of $Mg(OH)_2$ and consequently a white precipitate of $Mg(OH)_2$ is produced and equilibrium (2) is established.

$$Mg^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Mg(OH)_2(s) \text{ ----- (2)}$$

When NH_4C*l*(aq) is added, $[NH_4^+]$ in the solution increases. To counteract the increase in $[NH_4^+]$, the equilibrium position of reaction (1) shifts to the left, resulting in the decrease in $[OH^-]$.

This in turn causes the equilibrium position of reaction (2) to shift to the left, resulting in the dissolution of $Mg(OH)_2$.

With sufficient NH_4C*l*(aq) added, the ionic product, $[Mg^{2+}][OH^-]^2$, will be less than K_{sp} and hence all the $Mg(OH)_2(s)$ eventually dissolves completely to form a colourless solution.

(c) $NH_3(aq)$ is a weak base that undergoes partial ionisation in water to produce OH^- ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

When $NH_3(aq)$ is added to $Zn^{2+}(aq)$, the $[OH^-]$ in the Zn^{2+} solution is increased and this makes the ionic product, $[Zn^{2+}][OH^-]^2$, exceeds the K_{sp} of $Zn(OH)_2$ and consequently a white precipitate of $Zn(OH)_2$ is formed and equilibrium (1) is established.

$$Zn^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Zn(OH)_2(s) \text{ .....(1)}$$

When excess $NH_3(aq)$ is added, the complex ion, $[Zn(NH_3)_4]^{2+}$, is formed and equilibrium (2) is established.

$$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq) \text{ .....(2)}$$
colourless solution

The formation of $[Zn(NH_3)_4]^{2+}$ decreases the concentration of uncomplexed $Zn^{2+}(aq)$ ions in the solution.

To counteract the decrease in $[Zn^{2+}]$, the equilibrium position of reaction (1) shifts left, resulting in the dissolution of $Zn(OH)_2$ i.e. the white precipitate dissolves.

With sufficient $NH_3(aq)$ added, the ionic product, $[Zn^{2+}][OH^-]^2$, will be less than K_{sp} and hence all the $Zn(OH)_2$ eventually dissolves to form a colourless solution containing $[Zn(NH_3)_4]^{2+}$ ions.

9 *Reaction 1: KCl and $AgNO_3$*

$KCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + KNO_3(aq)$

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

Observation: White ppt of AgCl is formed.

Reaction 2: AgCl and NH_3

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ ----------(1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ----(2)

When $NH_3(aq)$ is added, the silver diammine complex, $[Ag(NH_3)_2]^+$, is formed and equilibrium (2) is established. The formation of $[Ag(NH_3)_2]^+$ decreases the concentration of uncomplexed Ag^+ in the solution.

To counteract the decrease in $[Ag^+]$, equilibrium position of reaction (1) shifts right, resulting in the dissolution of AgCl(s).

When sufficient $NH_3(aq)$ is added, the ionic product, $[Ag^+][Cl^-]$, will be less than K_{sp}, and all the white ppt of AgCl dissolves.

Observation: White ppt of AgCl dissolves in excess aqueous ammonia to form a colourless solution.

Reaction 3: NaBr and $AgNO_3$
$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s)$

When NaBr(aq) is added, the $[Br^-]$ in the solution is increased. When sufficient NaBr(aq) is added, the ionic product, $[Ag^+][Br^-]$, will exceed the K_{sp} of AgBr, and consequently a pale cream precipitate of AgBr is produced.

Observation: Pale cream ppt of AgBr is formed.

Reaction 4: AgBr dissolves in NaCN
$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ ----------(3)

When NaCN(aq), the complex ion, $[Ag(CN)_2]^-$, is formed and equilibrium (4) is established.

$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq)$ ----------(4)

This lowers the concentration of uncomplexed Ag^+ in the solution. To counteract the decrease in $[Ag^+]$, equilibrium position of reaction (3) shifts to the right causing more AgBr(s) to dissolve.

When sufficient NaCN(aq) has been added such that the ionic product of AgBr becomes smaller than its K_{sp}, all the cream ppt of AgBr dissolves.

Observation: Pale cream ppt of AgBr dissolves in excess aqueous sodium cyanide to form a colourless solution.