

Marks
8

- A solution is prepared that contains sodium chloride and sodium chromate (both 0.10 M). When a concentrated solution of silver nitrate is added slowly, white AgCl(s) begins to precipitate. After most of the Cl⁻(aq) has been consumed, red Ag₂CrO₄(s) starts to precipitate.

Ignoring dilution, what is the concentration of silver ions when silver chloride solid first starts to precipitate? K_{sp} (AgCl) is 1.8×10^{-10} .

K_{sp} refers to the dissolution reaction: $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

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

As $[\text{Cl}^-(\text{aq})] = 0.10 \text{ M}$, the minimum concentration of $\text{Ag}^+(\text{aq})$ required to ensure AgCl(s) is present is given by:

$$[\text{Ag}^+(\text{aq})] = K_{sp}(\text{AgCl}) / [\text{Cl}^-(\text{aq})] = (1.8 \times 10^{-10} / 0.10) \text{ M} = 1.8 \times 10^{-9} \text{ M}$$

Answer: $1.8 \times 10^{-9} \text{ M}$

Ignoring dilution, what is the concentration of silver ions when silver chromate solid first starts to precipitate? K_{sp} (Ag₂CrO₄) is 3.6×10^{-12} .

K_{sp} refers to the dissolution reaction: $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+(\text{aq})]^2[\text{CrO}_4^{2-}(\text{aq})]$$

As $[\text{CrO}_4^{2-}(\text{aq})] = 0.10 \text{ M}$, precipitation of Ag₂CrO₄(s) will occur when:

$$[\text{Ag}^+(\text{aq})]^2 = K_{sp}(\text{Ag}_2\text{CrO}_4) / [\text{CrO}_4^{2-}] = (3.6 \times 10^{-12} / 0.10) \text{ M} = 3.6 \times 10^{-11} \text{ M}$$

$$[\text{Ag}^+(\text{aq})] = 6.0 \times 10^{-6} \text{ M}$$

Answer: $6.0 \times 10^{-6} \text{ M}$

What is the concentration of chloride ions when silver chromate solid first starts to precipitate?

As $[\text{Ag}^+(\text{aq})] = 6.0 \times 10^{-6} \text{ M}$ when silver chromate starts to precipitate, the concentration of Cl⁻(aq) is given by:

$$\begin{aligned} [\text{Cl}^-(\text{aq})] &= K_{sp}(\text{AgCl}) / [\text{Ag}^+(\text{aq})] = (1.8 \times 10^{-10} / 6.0 \times 10^{-6}) \text{ M} = 1.8 \times 10^{-9} \text{ M} \\ &= 3.0 \times 10^{-5} \text{ M} \end{aligned}$$

Answer: $3.0 \times 10^{-5} \text{ M}$

ANSWER CONTINUES ON THE NEXT PAGE

What percentage of the chloride ion is precipitated before any silver chromate is precipitated?

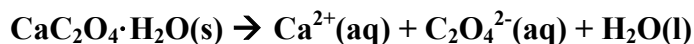
When silver chromate first precipitates, $[\text{Cl}^-(\text{aq})] = 3.0 \times 10^{-5} \text{ M}$. Initially, $[\text{Cl}^-(\text{aq})] = 0.10 \text{ M}$ so the percentage that has precipitated as $\text{AgCl}(\text{s})$ at this point is:

$$\text{percentage precipitated} = \frac{(0.10 - 3.0 \times 10^{-5})}{0.10} \times 100\% = 99.97\%$$

Answer: **99.97%**

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- The salt calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp} .



$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})]$$

What is the molar solubility of calcium oxalate? $K_{\text{sp}} = 2.3 \times 10^{-9}$

If x mol of the salt dissolves in one litre, then the molar solubility is x M. If x mol dissolves in one litre then $[\text{Ca}^{2+}(\text{aq})] = x$ M and $[\text{C}_2\text{O}_4^{2-}(\text{aq})] = x$ M.

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})] = (x)(x) = x^2 = 2.3 \times 10^{-9}$$

$$x = 4.8 \times 10^{-5} \text{ mol L}^{-1}$$

Answer: $4.8 \times 10^{-5} \text{ mol L}^{-1}$

If additional calcium oxalate is added to a saturated solution, what is the effect on $[\text{Ca}^{2+}(\text{aq})]$?

A saturated solid has the maximum possible dissolution. Adding additional solid has no effect on the equilibrium and so no effect on $[\text{Ca}^{2+}(\text{aq})]$.

Following blood donation, a solution of sodium oxalate is added to remove $\text{Ca}^{2+}(\text{aq})$ ions which cause the blood to clot. The concentration of $\text{Ca}^{2+}(\text{aq})$ ions in blood is $9.7 \times 10^{-5} \text{ g mL}^{-1}$. If 100.0 mL of 0.1550 M $\text{Na}_2\text{C}_2\text{O}_4$ is added to 100.0 mL of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

The amount of Ca^{2+} present in 100.0 mL is $9.7 \times 10^{-3} \text{ g}$. As its molar mass is 40.08 g mol^{-1} , this corresponds to:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} = \\ &= (9.7 \times 10^{-3} \text{ g}) / (40.08 \text{ g mol}^{-1}) = 2.4 \times 10^{-4} \text{ mol} \end{aligned}$$

The number of moles of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ added is:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.1550 \text{ mol L}^{-1}) \times (0.1000 \text{ L}) = 0.01550 \text{ mol} \end{aligned}$$

The amount of $\text{C}_2\text{O}_4^{2-}$ is *much* larger than the amount of Ca^{2+} present so precipitation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ does not reduce the $\text{C}_2\text{O}_4^{2-}$ significantly.

When the oxalate is added to the blood, the total volume increases to $(100.0 + 100.0) \text{ mL} = 200.0 \text{ mL}$. The concentration of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ is now:

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$$\begin{aligned}\text{concentration} &= \text{number of moles} / \text{volume} \\ &= (0.01550 \text{ mol}) / (0.2000 \text{ L}) = 0.0775 \text{ mol L}^{-1}\end{aligned}$$

Using $K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})]$:

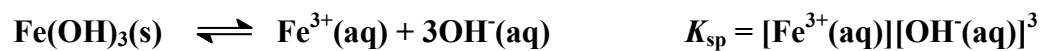
$$[\text{Ca}^{2+}(\text{aq})] = K_{\text{sp}} / [\text{C}_2\text{O}_4^{2-}(\text{aq})] = (2.3 \times 10^{-9} / 0.0775) \text{ M} = 3.0 \times 10^{-8} \text{ M}$$

Answer: $3.0 \times 10^{-8} \text{ M}$

- The K_{sp} for $\text{Fe}(\text{OH})_3$ is 2.64×10^{-39} . What is its molar solubility in water?

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The dissolution reaction and its equilibrium constant expression are:



The molar solubility is the number of moles that dissolve in a litre. If s mol dissolves in a litre:

$$[\text{Fe}^{3+}(\text{aq})] = s \text{ M} \quad \text{and} \quad [\text{OH}^{-}(\text{aq})] = 3s \text{ M}$$

Hence:

$$K_{\text{sp}} = (s)(3s)^3 = 27s^4 = 2.64 \times 10^{-39}$$

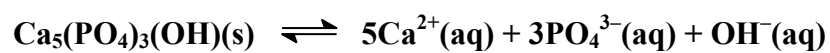
so

$$s = 9.94 \times 10^{-11} \text{ M}$$

Answer: $9.94 \times 10^{-11} \text{ M}$

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- Give the equation for the dissolution of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, in water.



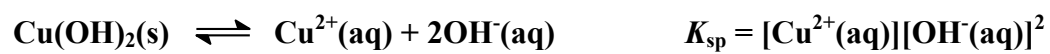
What is the formula for the solubility product constant for hydroxyapatite?

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})]^5 [\text{PO}_4^{3-}(\text{aq})]^3 [\text{OH}^{-}(\text{aq})]$$

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- What is the solubility of $\text{Cu}(\text{OH})_2$ in mol L^{-1} ? K_{sp} ($\text{Cu}(\text{OH})_2$) is 1.6×10^{-19} at 25°C .

The dissolution reaction and associated solubility product are:



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

$$K_{\text{sp}} = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-19}$$

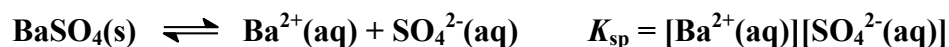
$$x = 3.4 \times 10^{-7} \text{ M}$$

Answer: $3.4 \times 10^{-7} \text{ M}$

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- BaSO₄ is used as a contrast agent in medical imaging. It has a K_{sp} of 1.1×10^{-10} . What is the molarity of Ba²⁺ ions in a saturated aqueous solution of BaSO₄?

The dissolution reaction is:



From the reaction, $[\text{Ba}^{2+}(\text{aq})] = [\text{SO}_4^{2-}(\text{aq})]$. Hence if $[\text{Ba}^{2+}(\text{aq})] = S$:

$$S^2 = K_{sp} = 1.1 \times 10^{-10}$$
$$S = 1.0 \times 10^{-5} \text{ M}$$

Answer: $1.0 \times 10^{-5} \text{ M}$

What is the molar solubility of BaSO₄ in the presence of a 0.1 M solution of Na₂SO₄?

The added SO₄²⁻ will dominate over that produced in the dissolution reaction so $[\text{SO}_4^{2-}(\text{aq})] = 0.1 \text{ M}$. For the dissolution reaction to still be at equilibrium:

$$K_{sp} = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = 1.1 \times 10^{-10}$$

With $[\text{SO}_4^{2-}(\text{aq})] = 0.1 \text{ M}$,

$$[\text{Ba}^{2+}(\text{aq})] = K_{sp} / [\text{SO}_4^{2-}(\text{aq})] = 1.1 \times 10^{-10} / 0.1 \text{ M} = 1 \times 10^{-9} \text{ M}$$

Answer: $1 \times 10^{-9} \text{ M}$

The lethal concentration of Ba²⁺ in humans is about 60 mg L⁻¹ ($4 \times 10^{-4} \text{ M}$). Is there any advantage to administering BaSO₄ in the presence of 0.1 M Na₂SO₄ solution? Explain your reasoning.

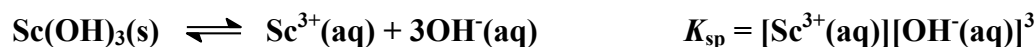
No. The lethal $[\text{Ba}^{2+}(\text{aq})]$ is 40 times greater than the $[\text{Ba}^{2+}(\text{aq})]$ in normal aqueous solution.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

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- What is the solubility of scandium hydroxide, $\text{Sc}(\text{OH})_3$, ($K_{\text{sp}} = 2 \times 10^{-30}$) in water? Give your answer in g per 100 mL.

The dissolution reaction and solubility product are:



If S mol in one litre, $[\text{Sc}^{3+}(\text{aq})] = S$ M and $[\text{OH}^{-}(\text{aq})] = 3S$ M. Hence:

$$K_{\text{sp}} = (S)(3S)^3 = 27S^4 = 2 \times 10^{-30}$$

$$S = 1.6 \times 10^{-8} \text{ M}$$

This is the number of moles that dissolve in one litre. The number of moles that dissolve in 100 mL is therefore 1.6×10^{-9} mol.

The molar mass of $\text{Sc}(\text{OH})_3$ is:

$$\begin{aligned} \text{molar mass} &= (44.96 \text{ (Sc)} + 3 \times 16.00 \text{ (O)} + 3 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} \\ &= 95.984 \text{ g mol}^{-1} \end{aligned}$$

The mass corresponding to 1.6×10^{-9} mol is therefore:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{molar mass} \\ &= (1.6 \times 10^{-9} \text{ mol}) \times (95.984 \text{ g mol}^{-1}) = 1.6 \times 10^{-7} \text{ g} \end{aligned}$$

The solubility is 1.6×10^{-7} g per 100 mL.

Answer: 1.6×10^{-7} g per 100 mL

- How does the interplay of ΔH and ΔS affect the spontaneity of the phase change between solid and liquid water?

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$$\Delta G = \Delta H - T\Delta S$$

Any process is spontaneous if $\Delta G < 0$, i.e. if $T\Delta S > \Delta H$.

For the melting of ice, both ΔS and ΔH are positive, so this process is spontaneous at higher temperatures.

Conversely, for the freezing of water, both ΔS and ΔH are negative, so this process is spontaneous at lower temperatures.

- Following blood donation, a solution of sodium oxalate is added to remove Ca^{2+} ions (as calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $K_{\text{sp}} 2.3 \times 10^{-9}$), which cause the blood to clot. If the concentration of Ca^{2+} ions in blood is $9.7 \times 10^{-5} \text{ g mL}^{-1}$, and 100.0 mL of 0.1550 M $\text{Na}_2\text{C}_2\text{O}_4$ is added to a 104 mL sample of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

The amount of Ca^{2+} present in 100.0 mL is $9.7 \times 10^{-3} \text{ g}$. As its molar mass is 40.08 g mol^{-1} , this corresponds to:

$$\begin{aligned}\text{number of moles} &= \text{mass} / \text{molar mass} = \\ &= (9.7 \times 10^{-3} \text{ g}) / (40.08 \text{ g mol}^{-1}) = 2.4 \times 10^{-4} \text{ mol}\end{aligned}$$

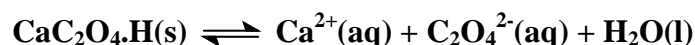
The number of moles of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ added is:

$$\begin{aligned}\text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.1550 \text{ mol L}^{-1}) \times (0.1000 \text{ L}) = 0.01550 \text{ mol}\end{aligned}$$

When this is added to the blood, the total volume increases to $(100.0 + 104) \text{ mL} = 204 \text{ mL}$. The concentration of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ is now:

$$\begin{aligned}\text{concentration} &= \text{number of moles} / \text{volume} \\ &= (0.01550 \text{ mol}) / (0.204 \text{ L}) = 0.0760 \text{ mol L}^{-1}\end{aligned}$$

For $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$, the solubility product is for the reaction:



$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})]$$

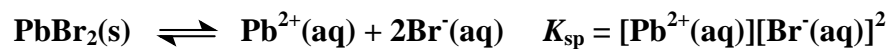
The amount of $\text{C}_2\text{O}_4^{2-}$ is *much* larger than the amount of Ca^{2+} present so precipitation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ does not reduce its concentration significantly. Hence:

$$[\text{Ca}^{2+}(\text{aq})] = K_{\text{sp}} / [\text{C}_2\text{O}_4^{2-}(\text{aq})] = (2.3 \times 10^{-9} / 0.0760) \text{ M} = 3.0 \times 10^{-8} \text{ M}$$

Answer: $3.0 \times 10^{-8} \text{ M}$

- Calculate the molar solubility of lead bromide given that its solubility product constant, K_{sp} , is 2.1×10^{-6} .

The dissolution equilibrium and solubility product are:



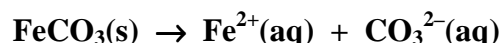
From the chemical equation, if s mol of dissolves in 1.0 L, $[\text{Pb}^{2+}(\text{aq})] = s$ M and $[\text{Br}^{-}(\text{aq})] = 2s$ M. Hence:

$$K_{sp} = (s)(2s)^2 = 4s^3 = 2.1 \times 10^{-6} \text{ or } s = 8.1 \times 10^{-3} \text{ M}$$

Answer: **$8.1 \times 10^{-3} \text{ M}$**

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- Write a balanced chemical equation representing the dissolution of FeCO_3 in water at pH 7.



Ignoring any hydrolysis of the ions, calculate the solubility (in g L^{-1}) of FeCO_3 in water at pH 7. The solubility product constant, K_{sp} , for FeCO_3 is 2.1×10^{-11} .

From the equation above, $K_{\text{sp}} = [\text{Fe}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})]$. If s mol of FeCO_3 dissolves in 1.0 L, $[\text{Fe}^{2+}(\text{aq})] = [\text{CO}_3^{2-}(\text{aq})] = s$ M. Hence:

$$K_{\text{sp}} = [\text{Fe}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = (s)(s) = s^2 = 2.1 \times 10^{-11} \text{ or } s = 4.6 \times 10^{-6} \text{ M}$$

The formula mass of FeCO_3 is $(55.85 (\text{Fe}) + 12.01 (\text{C}) + 3 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 115.86 \text{ g mol}^{-1}$. From above, 4.6×10^{-6} mol of FeCO_3 dissolves in 1.0 L. This corresponds to:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{formula mass} \\ &= (4.6 \times 10^{-6} \text{ mol}) \times (115.86 \text{ g mol}^{-1}) = 5.3 \times 10^{-4} \text{ g} \end{aligned}$$

This is the mass that dissolves in 1.0 L. The solubility is $5.3 \times 10^{-4} \text{ g L}^{-1}$.

Answer: $5.3 \times 10^{-4} \text{ g L}^{-1}$

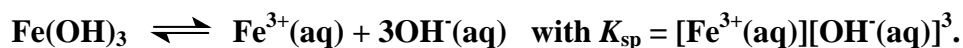
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- The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. The pH of the oceans before the Industrial Revolution was around 8.22. What was the maximum concentration of $\text{Fe}^{3+}(\text{aq})$ in the ocean at this pH? The K_{sp} of $\text{Fe}(\text{OH})_3$ is 1×10^{-39} .

As $\text{pH} + \text{pOH} = 14.00$, $\text{pOH} = 14.00 - 8.22 = 5.78$.

By definition, $\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})]$ and so $[\text{OH}^-(\text{aq})] = 10^{-5.78}$.

$\text{Fe}(\text{OH})_3$ dissolves according to the equilibrium:



As $K_{\text{sp}} = 1 \times 10^{-39}$ and $[\text{OH}^-(\text{aq})] = 10^{-5.78}$:

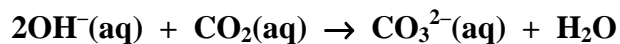
$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^3 = (1 \times 10^{-39}) / (10^{-5.78})^3 = 2 \times 10^{-22} \text{ M}$$

Answer: $2 \times 10^{-22} \text{ M}$

ANSWER CONTINUES ON THE NEXT PAGE

Industrialisation has led to an increase in atmospheric CO₂. What effect has this had on the amount of Fe³⁺(aq) in sea water?

CO₂ dissolves in water to give acidic solution that reacts with OH⁻ ions.



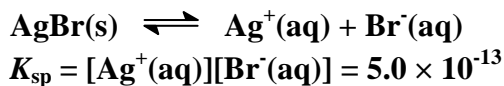
From Le Chatelier's principle, the decrease in [OH⁻(aq)] will result in an increase in [Fe³⁺(aq)].

Equivalently, if [OH⁻(aq)] is decreased, [Fe³⁺(aq)] must increase as K_{sp} is a constant.

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A solution is prepared that is 0.10 M in potassium bromide and 0.10 M in potassium chromate. A concentrated aqueous solution of silver nitrate is added with stirring. What is the concentration of $\text{Ag}^+(\text{aq})$ ions when silver bromide first appears?
 K_{sp} of $\text{AgBr} = 5.0 \times 10^{-13}$

When precipitation occurs, the following equilibrium is established and $[\text{Ag}^+(\text{aq})]$ and $[\text{Br}^-(\text{aq})]$ are controlled by the value of the solubility product:



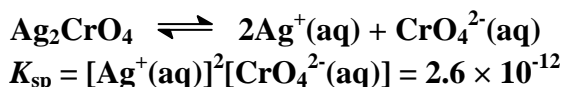
As the solution is 0.10 M in KBr, $[\text{Br}^-(\text{aq})] = 0.10 \text{ M}$:

$$[\text{Ag}^+(\text{aq})] \times (0.10) = 5.0 \times 10^{-13} \quad \text{so } [\text{Ag}^+(\text{aq})] = 5.0 \times 10^{-12} \text{ M}$$

Answer: $5.0 \times 10^{-12} \text{ M}$

What is the concentration of $\text{Ag}^+(\text{aq})$ ions when silver chromate first appears?
 K_{sp} of $\text{Ag}_2\text{CrO}_4 = 2.6 \times 10^{-12}$

When precipitation occurs, the following equilibrium is established and $[\text{Ag}^+(\text{aq})]$ and $[\text{CrO}_4^{2-}(\text{aq})]$ are controlled by the value of the solubility product:



As the solution is 0.10 M in K_2CrO_4 , $[\text{CrO}_4^{2-}(\text{aq})] = 0.10 \text{ M}$:

$$[\text{Ag}^+(\text{aq})]^2 \times (0.10) = 2.6 \times 10^{-12} \quad \text{so } [\text{Ag}^+(\text{aq})] = 5.1 \times 10^{-6} \text{ M}$$

Answer: $5.1 \times 10^{-6} \text{ M}$

What is the concentration of $\text{Br}^-(\text{aq})$ ions when silver chromate first appears?

$[\text{Br}^-(\text{aq})]$ is control by the K_{sp} for AgBr and so when $[\text{Ag}^+(\text{aq})] = 5.1 \times 10^{-6} \text{ M}$,

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{Br}^-(\text{aq})] = 5.0 \times 10^{-13}$$

$$(5.1 \times 10^{-6}) \times [\text{Br}^-(\text{aq})] = 5.0 \times 10^{-13} \quad \text{so } [\text{Br}^-(\text{aq})] = 9.8 \times 10^{-8} \text{ M}$$

Answer: $9.8 \times 10^{-8} \text{ M}$

- The K_{sp} of $\text{Al}(\text{OH})_3$ is $1.0 \times 10^{-33} \text{ M}^4$. What is the solubility of $\text{Al}(\text{OH})_3$ in g L^{-1} ?

The solubility equilibrium is:



If the molar solubility = S then $[\text{Al}^{3+}(\text{aq})] = \text{S}$ and $[\text{OH}^{-}(\text{aq})] = 3\text{S}$. Hence:

$$K_{sp} = [\text{Al}^{3+}(\text{aq})][\text{OH}^{-}(\text{aq})] = (\text{S})(3\text{S})^3 = 27\text{S}^4 = 1.0 \times 10^{-33}$$

$$\text{Hence, } \text{S} = \sqrt[4]{\frac{1.0 \times 10^{-33}}{27}} = 2.5 \times 10^{-9} \text{ M}$$

The formula mass of $\text{Al}(\text{OH})_3$ is $(26.98 (\text{Al})) + 3 \times (16.00 (\text{O}) + 1.008 (\text{H})) = 78.004$

As mass = number of moles \times formula mass, the solubility in g L^{-1} is:

$$\text{solubility} = (2.5 \times 10^{-9}) \times (78.004) = 1.9 \times 10^{-7} \text{ g L}^{-1}$$

Answer: **$1.9 \times 10^{-7} \text{ g L}^{-1}$**

What is the solubility of $\text{Al}(\text{OH})_3$ in g L^{-1} at pH 4.00?

As $\text{pH} + \text{pOH} = 14.00$, $\text{pOH} = 14.00 - 4.00 = 10.00$.

As $\text{pOH} = -\log_{10}([\text{OH}^{-}(\text{aq})])$, $[\text{OH}^{-}(\text{aq})] = 10^{-10.00} \text{ M}$.

From above, $K_{sp} = [\text{Al}^{3+}(\text{aq})][\text{OH}^{-}(\text{aq})]$. If the molar solubility is S then:

$$K_{sp} = (\text{S}) \times (10^{-10.00})^3 = 1.0 \times 10^{-33} \text{ and so } \text{S} = 1.0 \times 10^{-3} \text{ M}$$

Converting the molar solubility into g L^{-1} gives:

$$\text{solubility} = (1.0 \times 10^{-3}) \times (78.004) = 0.078 \text{ g L}^{-1}$$

Answer: **0.078 g L^{-1}**

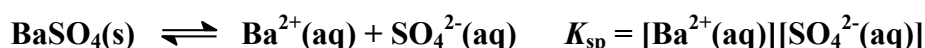
- Barium sulfate is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp} , for BaSO_4 , given that a maximum of 1.167×10^{-8} g will dissolve in 500 mL of water?

Marks
4

The formula mass of BaSO_4 is $137.34 (\text{Ba}) + 32.07 (\text{S}) + 4 \times 16.00 = 233.41 \text{ g mol}^{-1}$. 1.167×10^{-8} g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.167 \times 10^{-8}}{233.41} = 5.000 \times 10^{-11}$$

Barium sulfate dissolves according to the equilibrium:



As 5.000×10^{-11} mol dissolves in 500 mL,

$$[\text{Ba}^{2+}(\text{aq})] = [\text{SO}_4^{2-}(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.000 \times 10^{-11}}{0.500} = 1.00 \times 10^{-10} \text{ M}$$

Hence,

$$K_{sp} = (1.00 \times 10^{-10}) \times (1.00 \times 10^{-10}) = 1.00 \times 10^{-20}$$

Answer: 1.00×10^{-20}

What advantage would there be in administering BaSO_4 as a slurry that also contains 0.5 M Na_2SO_4 ?

As indicated by the very small solubility above, the equilibrium



lies far to the left. Adding more $\text{SO}_4^{2-}(\text{aq})$ ions pushes it further to the left.

This acts to remove $\text{Ba}^{2+}(\text{aq})$ ions from solution. This is advantageous as barium ions are highly toxic.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is used as treatment for excess acidity in the stomach. Its solubility product constant, K_{sp} , is $7.1 \times 10^{-12} \text{ M}^3$. Calculate the pH of a solution that is in equilibrium with $\text{Mg}(\text{OH})_2(\text{s})$.

The dissolution equilibrium is: $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$

Hence, $K_{\text{sp}} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2$

If $[\text{Mg}^{2+}(\text{aq})] = x$ then $[\text{OH}^{-}(\text{aq})] = 2x$ and $K_{\text{sp}} = (x)(2x)^2 = 4x^3$

As $K_{\text{sp}} = 7.1 \times 10^{-12}$, $x = 1.2 \times 10^{-4} \text{ M}$ and so $[\text{OH}^{-}(\text{aq})] = 2.4 \times 10^{-4} \text{ M}$

As $\text{pH} + \text{pOH} = 14.0$ and $\text{pOH} = -\log[\text{OH}^{-}(\text{aq})] = -\log(2.4 \times 10^{-4}) = 3.6$:

$$\text{pH} = 14.0 - 3.6 = 10.4$$

Answer: pH = 10.4

Determine whether 3.0 g of $\text{Mg}(\text{OH})_2$ will dissolve in 1.0 L of a solution buffered to a pH of 8.00.

If $\text{pH} = 8.00$ then $\text{pOH} = 14.00 - 8.00 = 6.00$. As $\text{pOH} = -\log[\text{OH}^{-}(\text{aq})]$:

$$[\text{OH}^{-}(\text{aq})] = 1.00 \times 10^{-6}.$$

As $K_{\text{sp}} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 = 7.1 \times 10^{-12}$, the $[\text{Mg}^{2+}(\text{aq})]$ is:

$$[\text{Mg}^{2+}(\text{aq})] = \frac{K_{\text{sp}}}{[\text{OH}^{-}(\text{aq})]^2} = \frac{7.1 \times 10^{-12}}{(1.00 \times 10^{-6})^2} = 7.1 \text{ M}$$

As 1 mol of $\text{Mg}(\text{OH})_2(\text{s})$ dissolves to give 1 mol of $[\text{Mg}^{2+}(\text{aq})]$, this is also the number of moles of $\text{Mg}(\text{OH})_2(\text{s})$ which dissolves.

The molar mass of $\text{Mg}(\text{OH})_2$ is $(24.31 \text{ (Mg)}) + 2 \times (16.00 \text{ (O)} + 1.008 \text{ (H)}) = 58.326$

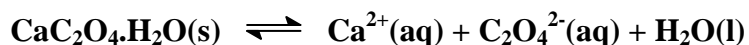
The mass of $\text{Mg}(\text{OH})_2$ which can dissolve is therefore $7.1 \times 58.326 = 410 \text{ g}$.

YES / NO

Marks
2

- Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, found in rhubarb, causes muscle spasms by precipitating Ca^{2+} ions from the blood as calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Given the solubility product constant for calcium oxalate is $2.3 \times 10^{-9} \text{ M}^2$, calculate the concentration of calcium ions in g L^{-1} formed by dissolving $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in water at 25°C to give a saturated solution.

The dissolution equilibrium for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is:



Hence, the solubility product $K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})]$

The chemical equation shows that dissolution of one mole of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ leads to one mole of $\text{Ca}^{2+}(\text{aq})$ and one mole of $\text{C}_2\text{O}_4^{2-}(\text{aq})$.

If $[\text{Ca}^{2+}(\text{aq})] = [\text{C}_2\text{O}_4^{2-}(\text{aq})] = x$,

$$K_{\text{sp}} = x^2 = 2.3 \times 10^{-9} \text{ so } x = 4.8 \times 10^{-5}.$$

Ca^{2+} will be present at $4.8 \times 10^{-5} \text{ mol L}^{-1}$. As the atomic mass of Ca is 40.08, this corresponds to a mass of:

$$\begin{aligned} \text{mass of } \text{Ca}^{2+} \text{ ions} &= \text{number of moles} \times \text{atomic mass} \\ &= (4.8 \times 10^{-5}) \times 40.08 = 1.9 \times 10^{-3} \text{ g} \end{aligned}$$

Answer: $1.9 \times 10^{-3} \text{ g}$

Marks
2

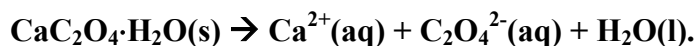
- Calcium oxalate is a major constituent of kidney stones. Calculate the solubility product constant for calcium oxalate given that a saturated solution of the salt can be made by dissolving 0.0061 g of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ in 1.0 L of water.

The molar mass of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is:

$$(40.08(\text{Ca}) + 2 \times 12.01(\text{C}) + 5 \times 16.00(\text{O}) + 2 \times 1.008(\text{H})) \text{ g mol}^{-1} = 146.116 \text{ g mol}^{-1}$$

Hence, 0.0061 g corresponds to $\frac{0.0061 \text{ g}}{146.116 \text{ g mol}^{-1}} = 4.2 \times 10^{-5} \text{ mol}$. As this amount dissolves in 1.0 L, the molar solubility = $S = 4.2 \times 10^{-5} \text{ M}$.

The dissolution equilibrium is:



As one mol of cation and one mol of anion is produced, the solubility product is:

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})] = (S)(S) = S^2 = (4.2 \times 10^{-5})^2 = 1.7 \times 10^{-9}$$

Answer: 1.7×10^{-9}

3

- A sample of 2.0 mg of $\text{Cu}(\text{OH})_2$ is added to 1.0 L of a solution buffered at a pH of 8.00. Will all of the $\text{Cu}(\text{OH})_2$ dissolve? Show all working. (The K_{sp} of $\text{Cu}(\text{OH})_2$ is $4.8 \times 10^{-20} \text{ M}^3$.)

As $\text{pH} + \text{pOH} = 14.00$, $\text{pOH} = 14.00 - 8.00 = 6.00$. Hence, $[\text{OH}^-(\text{aq})] = 10^{-6} \text{ M}$.

The dissolution equilibrium is: $\text{Cu}(\text{OH})_2(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

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

$$\text{As } K_{\text{sp}} = 4.8 \times 10^{-20}, S = \frac{4.8 \times 10^{-20}}{(10^{-6})^2} = 4.8 \times 10^{-8} \text{ M}$$

The molar mass of $\text{Cu}(\text{OH})_2$ is $(63.55 (\text{Cu}) + 2 \times (16.00 (\text{O}) + 1.008 (\text{O}))) \text{ g mol}^{-1} = 97.566 \text{ g mol}^{-1}$.

The solubility in g L^{-1} is therefore $(4.8 \times 10^{-8}) \times 97.566 = 4.7 \times 10^{-6}$.

Hence, only $4.7 \times 10^{-3} \text{ mg}$ will dissolve.

Answer: **NO**

Marks
6

- Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is used as treatment for excess acidity in the stomach. Calculate the pH of a solution that is in equilibrium with $\text{Mg}(\text{OH})_2$. The solubility product constant, K_{sp} of $\text{Mg}(\text{OH})_2$ is $7.1 \times 10^{-12} \text{ M}^2$.

The dissolution equilibrium is: $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$. As two mol of anion is produced for every one mol of cations, the expression for the solubility product is:

$$K_{\text{sp}} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 = (S) \times (2S)^2 = 4S^3 \text{ where } S \text{ is the molar solubility}$$

$$\text{Hence, } [\text{OH}^{-}(\text{aq})] = 2S = 2 \times \sqrt[3]{\frac{7.1 \times 10^{-12}}{4}} = 2.4 \times 10^{-4} \text{ M.}$$

$$\text{The pOH} = -\log_{10}[\text{OH}^{-}(\text{aq})] = -\log_{10}[2.4 \times 10^{-4}] = 3.6$$

$$\text{As pH} + \text{pOH} = 14.0, \text{ the pH} = 14.0 - 3.6 = 10.4$$

ANSWER: 10.4

Determine whether 2.0 g of $\text{Mg}(\text{OH})_2$ will dissolve in 1.0 L of a solution buffered to a pH of 7.00.

$$\text{At pH} = 7.00, \text{ pOH} = 14.00 - 7.00 = 7.00 \text{ and hence } [\text{OH}^{-}(\text{aq})] = 10^{-7} \text{ M.}$$

The formula mass of $\text{Mg}(\text{OH})_2$ is:

$$\begin{aligned} \text{formula mass} &= (24.31 \text{ (Mg)} + 2 \times (16.00 \text{ (O)} + 1.008 \text{ (H)})) \text{ g mol}^{-1} \\ &= 58.326 \text{ g mol}^{-1} \end{aligned}$$

Therefore 2.0 g contains:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{2.0 \text{ g}}{58.326 \text{ g mol}^{-1}} = 0.034 \text{ mol}$$

As each mole of $\text{Mg}(\text{OH})_2$ generates 1 mole of Mg^{2+} , if all of the $\text{Mg}(\text{OH})_2$ dissolves in 1.0 L of solution then $[\text{Mg}^{2+}(\text{aq})] = 0.034 \text{ M}$. The buffer removes the OH^{-} produced so that $[\text{OH}^{-}(\text{aq})] = 10^{-7} \text{ M}$.

The ionic product is then:

$$Q = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 = (0.034) \times (10^{-7})^2 = 3.4 \times 10^{-16}$$

As Q is much smaller than K_{sp} , all of the solid will dissolve.

ANSWER: YES / NO

Marks
3

- The solubility product constant of BaSO_4 is $1.1 \times 10^{-10} \text{ M}^2$. What is the solubility of BaSO_4 in g L^{-1} ?

The dissolution equilibrium is: $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$. As equal amounts of cations and anions are produced, the expression for the solubility product is:

$$K_{\text{sp}} = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = (S) \times (S) = S^2 \text{ where } S \text{ is the molar solubility.}$$

As $S^2 = 1.1 \times 10^{-10}$, the molar solubility = $S = 1.05 \times 10^{-5} \text{ M}$.

The formula mass of BaSO_4 is:

$$(137.34 (\text{Ba}) + 32.07 (\text{S}) + 4 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 228.41 \text{ g mol}^{-1}$$

Hence, the solubility is $(1.05 \times 10^{-5} \text{ M}) \times (228.41 \text{ g mol}^{-1}) = 2.4 \times 10^{-3} \text{ g L}^{-1}$

ANSWER: $2.4 \times 10^{-3} \text{ g L}^{-1}$

5

- The solubility product constant of Ag_2CrO_4 is $2.6 \times 10^{-12} \text{ M}^3$. What is the molar solubility of Ag_2CrO_4 in water?

The dissolution equilibrium is: $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$. As two mol of cation is produced for every one mol of anion, the expression for the solubility product is:

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})]^2 [\text{CrO}_4^{2-}(\text{aq})] = (2S)^2 \times (S) = 4S^3 \text{ where } S \text{ is the molar solubility.}$$

As $4S^3 = 2.6 \times 10^{-12} \text{ M}^3$, the molar solubility = $S = 8.7 \times 10^{-5} \text{ M}$.

ANSWER: $8.7 \times 10^{-5} \text{ M}$

What is the molar solubility of Ag_2CrO_4 in a solution of 0.10 M AgNO_3 ?

As AgNO_3 is very soluble, $[\text{Ag}^+(\text{aq})] = 0.10 \text{ M}$.

If S is the solubility, $K_{\text{sp}} = [\text{Ag}^+(\text{aq})]^2 [\text{CrO}_4^{2-}(\text{aq})] = (0.10)^2 \times S = 2.6 \times 10^{-12}$.

Hence, $S = 2.6 \times 10^{-10} \text{ M}$

ANSWER: $2.6 \times 10^{-10} \text{ M}$