

- Write the equation for the dissolution of lead(II) chloride, PbCl_2 , in water.



Write the expression for the solubility product constant, K_{sp} , for PbCl_2 .

$$K_{\text{sp}} = [\text{Pb}^{2+}(\text{aq})][\text{Cl}^{-}(\text{aq})]^2$$

What $[\text{Cl}^{-}]$ is needed to reduce the $[\text{Pb}^{2+}]$ to the maximum safe level of 0.015 mg L^{-1} ?
 $K_{\text{sp}}(\text{PbCl}_2) = 1.6 \times 10^{-6}$

The molar mass of Pb is 207.2 g mol^{-1} so 0.015 mg corresponds to:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= 0.015 \times 10^{-3} \text{ g} / 207.2 \text{ g mol}^{-1} = 7.2 \times 10^{-8} \text{ mol} \end{aligned}$$

The maximum safe value for $[\text{Pb}^{2+}(\text{aq})] = 7.2 \times 10^{-8} \text{ mol L}^{-1}$. As $K_{\text{sp}} = 1.6 \times 10^{-6}$, the value of $[\text{Cl}^{-}(\text{aq})]$ can be calculated:

$$K_{\text{sp}} = [\text{Pb}^{2+}(\text{aq})][\text{Cl}^{-}(\text{aq})]^2 = (7.2 \times 10^{-8}) \times [\text{Cl}^{-}(\text{aq})]^2 = 1.6 \times 10^{-6}$$

$$[\text{Cl}^{-}(\text{aq})] = 4.7 \text{ mol L}^{-1}$$

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The solubility of sodium chloride is 359 g L^{-1} . If a reservoir of $50,000 \text{ L}$ is saturated with lead(II) chloride, can sodium chloride be used to reduce the $[\text{Pb}^{2+}]$ to a safe level? If so, what mass of sodium chloride (in kg) would be needed?

The molar mass of NaCl is:

$$\text{molar mass} = (22.99 \text{ (Na)} + 35.45 \text{ (Cl)}) \text{ g mol}^{-1} = 58.44 \text{ g mol}^{-1}$$

359 g corresponds to:

$$\begin{aligned} \text{number of moles} &= \text{mass} / \text{molar mass} \\ &= 359 \text{ g} / 58.44 \text{ g mol}^{-1} = 6.14 \text{ mol} \end{aligned}$$

The maximum concentration of $[\text{Cl}^{-}(\text{aq})]$ from NaCl is therefore 6.14 mol L^{-1} . As this is greater than that required to keep the lead concentration at a safe level, it could be used.

The minimum concentration of $\text{Cl}^{-}(\text{aq})$ needed is 4.7 mol L^{-1} . The number of moles required to achieve this concentration in $50,000 \text{ L}$ is therefore:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= 4.7 \text{ mol L}^{-1} \times 50000 \text{ L} = 24000 \text{ mol} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

The mass of NaCl that corresponds to this is:

$$\begin{aligned}\text{mass} &= \text{number of moles} \times \text{molar mass} \\ &= 24000 \text{ mol} \times 58.44 \text{ g mol}^{-1} = 1.4 \times 10^7 \text{ g} = 14 \text{ tonnes}\end{aligned}$$

Answer: 1.4×10^7 g or 14 tonnes

Would the water in the reservoir be fit for drinking? Explain your answer.

It would be too salty to drink and is likely to exceed safe levels of $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$.

- The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. Write the chemical equation for the dissolution reaction of $\text{Fe}(\text{OH})_3$ in water.



What is the solubility of $\text{Fe}(\text{OH})_3$ in mol L^{-1} ? $K_{\text{sp}}(\text{Fe}(\text{OH})_3)$ is 2.8×10^{-39} at $25\text{ }^{\circ}\text{C}$.

From the chemical equation, $K_{\text{sp}} = [\text{Fe}^{3+}(\text{aq})][\text{OH}^{-}(\text{aq})]^3$.

If x mol of $\text{Fe}(\text{OH})_3$ dissolve in one litre, then $[\text{Fe}^{3+}(\text{aq})] = x$ and $[\text{OH}^{-}(\text{aq})] = 3x$. Hence,

$$K_{\text{sp}} = (x)(3x)^3 = 27x^4 = 2.8 \times 10^{-39}$$

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

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

Before the Industrial Revolution, the concentration of $\text{OH}^{-}(\text{aq})$ in the oceans was about $1.6 \times 10^{-6} \text{ M}$. What pH corresponds to this concentration at $25\text{ }^{\circ}\text{C}$?

If $[\text{OH}^{-}] = 1.6 \times 10^{-6} \text{ M}$, then by definition

$$\text{pOH} = -\log_{10}[\text{OH}^{-}(\text{aq})] = -\log_{10}(1.6 \times 10^{-6}) = 5.8$$

As $\text{pH} + \text{pOH} = 14.0$,

$$\text{pH} = 14.0 - 5.8 = 8.2$$

Answer: $\text{pH} = 8.2$

What is the solubility of $\text{Fe}(\text{OH})_3$ in mol L^{-1} at this pH?

As $[\text{OH}^{-}(\text{aq})] = 1.6 \times 10^{-6} \text{ M}$ and $K_{\text{sp}} = [\text{Fe}^{3+}(\text{aq})][\text{OH}^{-}(\text{aq})]^3$:

$$\begin{aligned} [\text{Fe}^{3+}(\text{aq})] &= K_{\text{sp}} / [\text{OH}^{-}(\text{aq})]^3 \\ &= 2.8 \times 10^{-39} / (1.6 \times 10^{-6})^3 \text{ M} \\ &= 6.8 \times 10^{-22} \text{ M} \end{aligned}$$

Answer: $6.8 \times 10^{-22} \text{ M}$

ANSWER CONTINUES OVER THE PAGE

Industrialisation has led to an increase in atmospheric CO₂. Predict the effect that this has had on the amount of Fe³⁺(aq) in sea water and briefly explain your answer.

Dissolved CO₂ reacts with water to form H₂CO₃ which is slightly acidic.



The increase in [H⁺(aq)] results in a decrease in [OH⁻(aq)] and hence (from Le Chatelier's principle) more Fe(OH)₃(s) will dissolve.

- Explain what is meant by the “common ion effect”.

The solubility of a salt is reduced by the presence of one of its constituent ions (the common ion) already in the solution. The presence of the common ion drives the equilibrium towards precipitation through Le Chatelier’s principle.

Magnesium hydroxide is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp} .



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

What is the molar solubility of magnesium hydroxide in water? $K_{sp} = 7.1 \times 10^{-12}$

The molar solubility is the number of the moles that dissolve per litre. From the chemical equation, if s mol of the solid dissolves in a litre, then:

$$\begin{aligned} [\text{Mg}^{2+}(\text{aq})] &= s \text{ M} \text{ and} \\ [\text{OH}^{-}(\text{aq})] &= 2s \text{ M} \end{aligned}$$

Hence,

$$K_{sp} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 = (s)(2s)^2 = 4s^3 = 7.1 \times 10^{-12}$$

$$s = 1.2 \times 10^{-4}$$

Answer: $1.2 \times 10^{-4} \text{ M}$

What is the pH of a saturated solution of magnesium hydroxide in water?

From above,

$$[\text{OH}^{-}(\text{aq})] = 2s \text{ M} = 2 \times (1.2 \times 10^{-4}) \text{ M} = 2.4 \times 10^{-4} \text{ M}$$

Hence,

$$\text{pOH} = -\log_{10}[\text{OH}^{-}(\text{aq})] = -\log_{10}(2.4 \times 10^{-4}) = 3.62$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.62 = 10.38$$

Answer: **10.38**

What is the molar solubility of magnesium hydroxide in a buffer solution at pH 9.24?

Marks
3

At pH 9.24,

$$\text{pOH} = 14.00 - 9.24 = 4.76$$

$$[\text{OH}^-(\text{aq})] = 10^{-\text{pOH}} = 10^{-4.76} \text{ M}$$

From 2012-N-6, $K_{\text{sp}} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^-(\text{aq})]^2$ so

$$[\text{Mg}^{2+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^2 = 7.1 \times 10^{-12} / (10^{-4.76})^2 = 0.024 \text{ M}$$

Answer: **0.024 M**

Do the relative solubilities of magnesium hydroxide in water and the buffer solution support the concept of the common ion effect? Explain your reasoning.

Yes. The $[\text{OH}^-(\text{aq})]$ in the saturated $\text{Mg}(\text{OH})_2$ solution is $2.4 \times 10^{-4} \text{ M}$, higher than the $[\text{OH}^-(\text{aq})]$ in the buffer solution which remains constant at $10^{-4.76} \text{ M}$, *i.e.* $1.7 \times 10^{-5} \text{ M}$.

Normally the solubility of a solid decreases because of a high concentration of one of its ions. In this situation, the opposite is observed. Regardless of how much $\text{Mg}(\text{OH})_2$ dissolves, the $[\text{OH}^-]$ remains below that seen in a saturated solution of $\text{Mg}(\text{OH})_2$. Therefore the solubility of $\text{Mg}(\text{OH})_2$ increases in this particular buffer.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Nickel metal can be extracted and recycled from mobile phone batteries. This process leads to solutions containing both $\text{Cu}^{2+}(\text{aq})$ and $\text{Ni}^{2+}(\text{aq})$ ions. Separation of these ions is achieved by adding tiny amounts of sulfide ions as the metal sulfides have low and very different solubilities: $K_{\text{sp}}(\text{CuS}) = 8 \times 10^{-34}$ and $K_{\text{sp}}(\text{NiS}) = 3 \times 10^{-19}$.

An aqueous solution has $[\text{Ni}^{2+}(\text{aq})] = 0.0100 \text{ M}$ and an unknown concentration of $\text{Cu}^{2+}(\text{aq})$ ions. $\text{S}^{2-}(\text{aq})$ ions are added in small increments. CuS begins to precipitate when $[\text{S}^{2-}(\text{aq})] = 8 \times 10^{-32} \text{ M}$. What was the original value of $[\text{Cu}^{2+}(\text{aq})]$?

The solubility of CuS is *much* lower than NiS as its K_{sp} value is *much* smaller. When CuS begins to precipitate, virtually none will be left in solution.

$\text{CuS}(\text{s})$ dissolves to give $\text{Cu}^{2+}(\text{aq})$ and $\text{S}^{2-}(\text{aq})$, so $K_{\text{sp}}(\text{CuS}) = [\text{Cu}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})]$.

As $K_{\text{sp}} = 8 \times 10^{-34}$ and precipitation occurs when $[\text{S}^{2-}(\text{aq})] = 8 \times 10^{-32} \text{ M}$,

$$[\text{Cu}^{2+}(\text{aq})] = K_{\text{sp}}(\text{CuS}) / [\text{S}^{2-}(\text{aq})] = (8 \times 10^{-34}) / (8 \times 10^{-32}) = 0.01 \text{ M}$$

Answer: **0.01 M**

At what $[\text{S}^{2-}(\text{aq})]$ will NiS precipitate?

$\text{NiS}(\text{s})$ dissolves to give $\text{Ni}^{2+}(\text{aq})$ and $\text{S}^{2-}(\text{aq})$, so $K_{\text{sp}}(\text{NiS}) = [\text{Ni}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})]$.

As $K_{\text{sp}} = 3 \times 10^{-19}$ and $[\text{Ni}^{2+}(\text{aq})] = 0.0100 \text{ M}$,

$$[\text{S}^{2-}(\text{aq})] = K_{\text{sp}}(\text{NiS}) / [\text{Ni}^{2+}(\text{aq})] = (3 \times 10^{-19}) / (0.0100) = 3 \times 10^{-17} \text{ M}$$

Answer: **$3 \times 10^{-17} \text{ M}$**

If the CuS formed is filtered off before any NiS precipitates, how pure will the NiS precipitate be?

From above, NiS precipitates when $[\text{S}^{2-}(\text{aq})] = 3 \times 10^{-17} \text{ M}$. At this concentration,

$$[\text{Cu}^{2+}(\text{aq})] = K_{\text{sp}}(\text{CuS}) / [\text{S}^{2-}(\text{aq})] = (8 \times 10^{-34}) / (3 \times 10^{-17}) = 3 \times 10^{-17} \text{ M}$$

When NiS starts to precipitate, $[\text{Ni}^{2+}(\text{aq})] = 0.0100 \text{ M}$ and $[\text{Cu}^{2+}(\text{aq})] = 3 \times 10^{-17} \text{ M}$.

The NiS that precipitates will contain *very little* Cu^{2+} : it will be *very pure*.

Answer: **100%**

Marks
6

- The pH of the ocean before the industrial revolution was around 8.22. Show that this pH corresponds to a concentration of $[\text{OH}^-(\text{aq})] = 1.7 \times 10^{-6} \text{ M}$.

By definition, $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$. Hence, a pH of 8.22 corresponds to:

$$[\text{H}^+] = 10^{-\text{pH}} \text{ M} = 10^{-8.22} \text{ M}$$

$[\text{H}^+(\text{aq})]$ and $[\text{OH}^-(\text{aq})]$ are linked through K_w . Assuming a temperature of 298 K,

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.00 \times 10^{-14}$$

Hence:

$$[\text{OH}^-] = K_w / [\text{H}^+(\text{aq})] = 1.00 \times 10^{-14} / 10^{-8.22} \text{ M} = 1.7 \times 10^{-6} \text{ M}$$

All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of the hydroxide, $\text{Fe}(\text{OH})_3$, which has a K_{sp} of only 1×10^{-39} . What was the maximum concentration of $\text{Fe}^{3+}(\text{aq})$ at a pH of 8.22?

$\text{Fe}(\text{OH})_3(\text{s})$ dissolves according to the chemical equation:



The solubility product is therefore given by:

$$K_{\text{sp}} = [\text{Fe}^{3+}(\text{aq})][\text{OH}^-(\text{aq})]^3$$

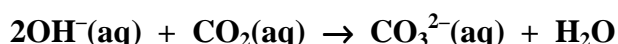
As $[\text{OH}^-(\text{aq})] = 1.7 \times 10^{-6} \text{ M}$:

$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^3 = 1 \times 10^{-39} / (1.7 \times 10^{-6})^3 \text{ M} = 2 \times 10^{-22} \text{ M}$$

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

Industrialisation has led to an increase in atmospheric CO_2 . What effect has this had on the amount of $\text{Fe}^{3+}(\text{aq})$ in sea water?

CO_2 dissolves in water to give acidic solution that reacts with OH^- ions.



Increased amounts of CO_2 is thus likely to decrease the amount of OH^- in the sea water. From Le Chatelier's principle, the decrease in $[\text{OH}^-]$ will result in the equilibrium for the dissolution of $\text{Fe}(\text{OH})_3$ above shifting to the right. This will lead to an increase in $[\text{Fe}^{3+}(\text{aq})]$.

- BaSO₄ is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp} , for BaSO₄, given that a maximum of 1.2×10^{-3} g dissolves in 500 mL of water.

The formula mass of BaSO₄ is:

$$137.34 (\text{Ba}) + 32.07 (\text{S}) + 4 \times 16.00 (\text{O}) = 233.44 \text{ g mol}^{-1}$$

A mass of 1.2×10^{-3} g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.2 \times 10^{-3} \text{ g}}{233.44 \text{ g mol}^{-1}} = 5.14 \times 10^{-6} \text{ mol}$$

The equation for the dissolution is:



If 5.14×10^{-6} mol dissolves, then the number of moles of Ba²⁺(aq) and SO₄²⁻(aq) will also be 5.14×10^{-6} mol. As these amounts are present in 500 mL of water:

$$[\text{Ba}^{2+}(\text{aq})] = [\text{SO}_4^{2-}(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.14 \times 10^{-6} \text{ mol}}{0.500 \text{ L}} = 1.03 \times 10^{-5} \text{ M}$$

Finally, the solubility product constant is:

$$K_{sp} = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = (1.03 \times 10^{-5})(1.03 \times 10^{-5}) = 1.1 \times 10^{-10}$$

Answer: 1.1×10^{-10}

Ba²⁺ ions are toxic. Comment on the suitability of BaSO₄ as a contrast agent.

As BaSO₄ has a very low solubility, [Ba²⁺(aq)] will be low and so very few of the toxic Ba²⁺ are actually dissolved into the blood stream.

What advantage would there be in administering BaSO₄ as a slurry which also contains 0.5 M Na₂SO₄?

The equilibrium,



will be shifted to the left by the addition of additional SO₄²⁻ from Na₂SO₄. This is an example of Le Châtelier's principle and is called the 'common ion effect'.

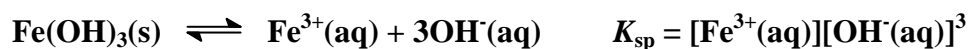
By shifting the reaction to the left, even less BaSO₄ will dissolve, reducing [Ba²⁺(aq)] to:

$$[\text{Ba}^{2+}(\text{aq})] = K_{sp} / [\text{SO}_4^{2-}(\text{aq})] = (1.1 \times 10^{-10}) / (0.5) = 2 \times 10^{-11} \text{ M}$$

This can be compared to the much higher value of 1×10^{-5} M calculated above.

- The K_{sp} of $\text{Fe}(\text{OH})_3$ is $2.0 \times 10^{-39} \text{ M}^4$. What is the solubility of $\text{Fe}(\text{OH})_3$ in g L^{-1} ?

The solubility equilibrium and constant for the dissolution of $\text{Fe}(\text{OH})_3$ are:



If S moles of $\text{Fe}(\text{OH})_3$ dissolve, S mol of $\text{Fe}^{3+}(\text{aq})$ and $3S$ mol of $\text{OH}^{-}(\text{aq})$ are formed. Thus,

$$K_{sp} = (S) \times (3S)^3 = 27S^4 = 2.0 \times 10^{-39}$$

$$S = 9.3 \times 10^{-11} \text{ M}$$

The formula mass of $\text{Fe}(\text{OH})_3$ is $(55.85 (\text{Fe}) + 3 \times (16.00 (\text{O}) + 1.008 (\text{H}))) \text{ g mol}^{-1} = 106.874 \text{ g mol}^{-1}$. Thus, as $9.3 \times 10^{-11} \text{ mol}$ dissolves in 1.0 L, the mass which dissolves in 1.0 L is:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{formula mass} \\ &= (9.3 \times 10^{-11} \text{ mol}) \times 106.874 \text{ g mol}^{-1} = 9.9 \times 10^{-9} \text{ g} \end{aligned}$$

Answer: $9.9 \times 10^{-9} \text{ g L}^{-1}$

What effect does lowering the pH have on the solubility of $\text{Fe}(\text{OH})_3$? Explain your answer.

The equilibrium for the reaction:



lies to the left. Addition of H^{+} removes the OH^{-} and hence, from Le Chatelier's principle more $\text{Fe}(\text{OH})_3(\text{s})$ will dissolve.

Hence, lowering the pH will increase the solubility.