

- Marks 6
- 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, Fe(OH)₃, which has a K_{sp} of only 2×10^{-39} .

Calculate the maximum possible concentration of $Fe^{3+}(aq)$ in the pre-industrial era ocean which had a pH of about 8.2.

When pH = 8.2, pOH = 14.0 – 8.2 = 5.8. As pOH = -log₁₀[OH⁻(aq)]: [OH⁻(aq)] = 10^{-5.8} M

 $Fe(OH)_3(s)$ dissolves according to the chemical equation:

$$Fe(OH)_3(s) \iff Fe^{3+}(aq) + 3OH^{-}(aq)$$

The solubility product is therefore given by:

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

As $[OH^{-}(aq)] = 10^{-5.8}$ M:

 $[Fe^{3+}(aq)] = K_{sp} / [OH^{-}(aq)]^{3} = 2 \times 10^{-39} / (10^{-5.8})^{3} M = 5 \times 10^{-22} M$

$$[\text{Fe}^{3+}(\text{aq})] = 5 \times 10^{-22} \text{ M}$$

How many Fe³⁺(aq) ions are present in a litre of seawater at this pH?

From above, $[Fe^{3+}(aq)] = 5 \times 10^{-22} \text{ M} = 5 \times 10^{-22} \text{ mol } L^{-1}$. Hence, a litre of seawater contains 5×10^{-22} mol.

The number of ions of Fe³⁺ is therefore:

number of ions = $(5 \times 10^{-22} \text{ mol}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 300$

Answer: 300

The pH of the ocean is predicted to drop to 7.8 by the end of this century as the concentration of CO_2 in the atmosphere increases. What percentage change in the concentration of $Fe^{3+}(aq)$ will result from this fall in pH?

When pH = 7.8, pOH = 14.0 – 7.8 = 6.2 and [OH⁻(aq)] = 10^{-6.2} M. Hence:

$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^{-}(\text{aq})]^{3} = 2 \times 10^{-39} / (10^{-6.2})^{3} \text{ M} = 8 \times 10^{-21} \text{ M}$$

The percentage increase is therefore:

percentage change =
$$\frac{(8 \times 10^{-21} - 5 \times 10^{-21})}{5 \times 10^{-21}} \times 100 \% = 1500 \%$$

Answer: 1500 %

Marks 4

• The ocean contains a variety of forms of CO_3^{2-} and CO_2 with a variety of acid-base and solubility equilibria determining their concentrations. There is concern that increasing levels of CO₂ will lead to increased dissolution of CaCO₃ and critically affect the survival of life forms that rely on a carbonaceous skeleton. Calculate the concentrations of Ca^{2+} and CO_3^{2-} in a saturated solution of CaCO₃. (The K_{sp} of CaCO₃ is 3.3×10^{-9} .) The dissolution of CaCO₃ follows the reaction, $CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$ If the molar solubility of CaCO₃ is S then $[Ca^{2+}(aq)] = [CO_3^{2-}(aq)] = S$. The solubility product is given by: $K_{sp} = [Ca^{2+}(aq)][CO_3^{2-}(aq)] = (S).(S) = S^2$ As $K_{\rm sp} = 3.3 \times 10^{-9}$, $S^2 = 3.3 \times 10^{-9}$ or $S = 5.7 \times 10^{-5}$ M $[CO_3^{2-}] = 5.7 \times 10^{-5} M$ $[Ca^{2+}] = 5.7 \times 10^{-5} M$ Calculate the pH of such a solution. (The pK_a of HCO₃⁻ is 10.33). CO_3^{2-} is a weak base and will react with water to produce HCO_3^{--} : CO_{3}^{2} HCO₃ H₂O OH. _

initial	5.7×10^{-5}	large	0	0
change	- <i>x</i>	negligible	+ <i>x</i>	+ <i>x</i>
final	$5.7 \times 10^{-5} - x$	large	x	x

The equilibrium constant K_b is given by:

$$K_{\rm b} = \frac{[\rm OH^{-}(aq)][\rm HCO_{3}^{-}(aq)]}{[\rm CO_{3}^{2-}(aq)]} = \frac{x^2}{5.7 \times 10^{-5} - x}$$

As $pK_a + pK_b = 14.00$, $pK_b = 14.00 - 10.33 = 3.67$. As $pK_b = -\log K_b$, so

$$K_{\rm b} = 10^{-3.67}$$
.

ANSWER CONTINUES ON THE NEXT PAGE

As the concentration of the base is so small, the 'small x' approximation cannot be used and it is necessary to solve the quadratic equation. From above,

 $x^{2} + 10^{-3.67}x - (5.7 \times 10^{-5} \times 10^{-3.67}) = 0$

Solving this using the quadratic formula gives $x = 4.67 \times 10^{-5} = [OH^{-1}(aq)]$. Hence,

 $pOH = -log_{10}[OH^{-}(aq)] = 4.33$

Finally, since pH + pOH = 14.00,

pH = 14.00 - 4.33 = 9.67

pH = **9.67**

THIS QUESTION CONTINUES ON THE NEXT PAGE

2008-N-3

The pH of surface ocean water is currently 8.10 (having fallen from a pre-industrial era level of 8.16), the concentration of HCO_3^{-1} is 2.5×10^{-3} M, and it is saturated with CaCO₃. Calculate the concentration of Ca²⁺ in these conditions.



The pH is expected to drop to about 7.8 by the end of the century as CO_2 levels increase further. What effect will this have on the solubility of $CaCO_3$ in sea water? Use chemical equations to assist with explaining your answer.

The solubility of CaCO₃ will increase.

At a lower pH, [OH⁻(aq)] will be lower. The equilibrium below will be shifted to the right:

 $CO_3^{2}(aq) + H_2O(l) \iff OH(aq) + HCO_3(aq)$

With lower $[CO_3^{2-}(aq)]$, $[Ca^{2+}(aq)]$ will increase as $[Ca^{2+}(aq)] = K_{sp} / [CO_3^{2-}(aq)]$. The solubility will be increased.

Marks

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• In order to reduce the incidence of dental cavities, water is fluoridated to a level of 1 mg L^{-1} . In regions where the water is "hard" the calcium concentration is typically 100 mg L⁻¹. Given that the K_{sp} of calcium fluoride is $3.9 \times 10^{-11} \text{ M}^3$, would it precipitate in these conditions? Show all working.

For the dissolution of $CaF_2(s) \iff Ca^{2+}(aq) + 2F'(aq), Q_{sp} = [Ca^{2+}(aq)][F'(aq)]^2$. If $Q_{sp} > K_{sp}$, then $CaF_2(s)$ will precipitate. If $Q_{sp} < K_{sp}$, then $CaF_2(s)$ will completely dissolve.

The atomic mass of calcium is 40.08 g mol⁻¹. A 100 mg L⁻¹ solution contains $\frac{100 \times 10^{-3}}{40.08}$ mol and has a concentration of $\frac{100 \times 10^{-3}}{40.08}$ M. [Ca²⁺(aq)] = 2.495 × 10⁻³ M.

The atomic mass of fluorine is 19.00 g mol⁻¹. A 1 mg L⁻¹ solution contains $\frac{1 \times 10^{-3}}{19.00}$ mol and has a concentration of $\frac{1 \times 10^{-3}}{19.00}$ M. [F⁻(aq)] = 5.263 × 10⁻⁵ M.

Hence, $Q_{sp} = (2.495 \times 10^{-3} \text{ M}) \times (5.263 \times 10^{-5} \text{ M})^2 = 6.911 \times 10^{-12} \text{ M}^3$. As $Q_{sp} < K_{sp}$, calcium fluoride will not precipitate.

Answer: No, it does not precipitate

• 2.00 g of solid calcium hydroxide is added to 1.00 L of water. What proportion of the calcium hydroxide remains undissolved when the system has reached equilibrium? $K_{\rm sp}({\rm Ca(OH)_2}) = 6.5 \times 10^{-6} {\rm M}^3$

The formula mass of $Ca(OH)_2$ is $(40.08 Ca)) + 2 \times (16.00 (O) + 1.008 (H)) = 74.096$. 2.00 g of $Ca(OH)_2$ therefore corresponds to:

amount of $Ca(OH)_2 = \frac{mass}{formula mass} = \frac{2.00}{74.096} = 0.0270 \text{ mol}$

The solubility equilibrium and constant are given by:

 $Ca(OH)_2 \iff Ca^{2+}(aq) + 2OH^{-}(aq) \quad K_{sp} = [Ca^{2+}(aq)][OH^{-}(aq)]^2$

If S mol dissolves in 1.00 L then $[Ca^{2+}(aq)] = S$ and $[OH^{-}(aq)] = 2S$. Thus,

 $K_{sp} = (S)(2S)^2 = 4S^3 = 6.5 \ 8 \ 10^{-6}$ so $S = 0.0118 \ mol$

The amount that remains undissolved is (0.0270) - (0.0118) = 0.0152 mol. The proportion that is undissolved is $\frac{0.0152}{0.0270} \times 100\% = 56\%$.

Answer: **56%**

What volume (in mL) of 10.0 M nitric acid must be added to this mixture in order to just dissolve all of the calcium hydroxide? Assume the volume of the nitric acid is small and can be ignored in the calculation of the total volume.

If all of the $Ca(OH)_2$ dissolves then $[Ca^{2+}(aq)] = 0.0270$ M. The [OH(aq)] required to achieve this is given by:

 $K_{sp} = [Ca^{2+}(aq)][OH^{-}(aq)]^{2} = (0.0270) \times [OH^{-}(aq)]^{2} = 6.5 \times 10^{-6}$ $[OH^{-}(aq)] = 0.0155 \text{ M}$

As dissolution of 0.0270 mol of $Ca(OH)_2$ produces $(2 \times 0.0270) = 0.0540$ mol of OH, the remainder has been neutralized by the added nitric acid:

number of moles of nitric acid added = 0.0540 - 0.0155 = 0.0384 mol

The volume of 10.0 M nitric acid which contains this amount is given by:

volume of nitric acid =
$$\frac{\text{number of moles}}{\text{concentration}} = \frac{0.0384}{10.0} = 3.84 \times 10^{-3} \text{ L} = 3.84 \text{ mL}$$

Answer: 3.84 mL

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Marks • Calcium oxalate is a major constituent of kidney stones. Calculate the solubility 2 product constant for calcium oxalate given that a saturated solution of the salt can be made by dissolving 0.0061 g of $CaC_2O_4 \cdot H_2O(s)$ in 1.0 L of water. The molar mass of CaC₂O₄·H₂O is: $(40.08(Ca) + 2 \times 12.01(C) + 5 \times 16.00(O) + 2 \times 1.008(H))$ g mol⁻¹ = 146.116 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 = $S = 4.2 \times 10^{-5}$ M. The dissolution equilibrium is: $CaC_2O_4 \cdot H_2O(s) \rightarrow Ca^{2+}(aq) + C_2O_4^{2-}(aq) + H_2O(l).$ As one mol of cation and one mol of anion is produced, the solubility product is: $K_{sp} = [Ca^{2+}(aq)][C_2O_4^{2-}(aq)] = (S)(S) = S^2 = (4.2 \times 10^{-5})^2 = 1.7 \times 10^{-9}$ Answer: 1.7×10^{-9} 3 A sample of 2.0 mg of Cu(OH)₂ is added to 1.0 L of a solution buffered at a pH of 8.00. Will all of the Cu(OH)₂ dissolve? Show all working. (The K_{sp} of Cu(OH)₂ is 4.8×10^{-20} M³.) As pH + pOH = 14.00, pOH = 14.00 - 8.00 = 6.00. Hence, $[OH^{-}(aq)] = 10^{-6}$ M. The dissolution equilibrium is: $Cu(OH)_2(s) \rightarrow Cu^{2+}(aq) + 2OH^{-}(aq)$ Hence, if S is the molar solubility, $K_{sp} = [Cu^{2+}(aq)][OH^{-}(aq)]^{2} = S \times [OH^{-}(aq)]^{2}$. As $K_{\rm sp} = 4.8 \times 10^{-20}$, $S = \frac{4.8 \times 10^{-20}}{(10^{-6})^2} = 4.8 \times 10^{-8} \,\mathrm{M}$

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

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

Hence, only 4.7×10^{-3} mg will dissolve.

Answer: NO

In the presence of excess hydroxide ion, Mg^{2+} can be precipitated as $Mg(OH)_2(s)$. What amount (in mol) of solid sodium hydroxide must be added to a 0.10 M solution of $Mg(NO_3)_2$ to just cause precipitation of $Mg(OH)_2(s)$. The solubility product constant of $Mg(OH)_2$ is $7.1 \times 10^{-12} \text{ M}^3$.

The solubility equilibrium and product for Mg(OH)₂(s) are:

$$Mg(OH)_2(s) \iff Mg^{2+}(aq) + 2OH^{-}(aq) \qquad K_{sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2$$

With [Mg²⁺(aq)] = 0.10 M, precipitation will occur when:

$$[OH^{-}(aq)]^{2} \ge \frac{K_{sp}}{[Mg^{2+}(aq)]} = \frac{(7.1 \times 10^{-12})}{(0.10)}$$
 so $[OH^{-}(aq)] \ge 8.4 \times 10^{-6} \text{ M}$

(As the volume of the solution is not specified, the number of moles of NaOH(s) cannot be given. A 1 L solution would require 8.4×10^{-6} mol.)

ANSWER: **8.4** × 10⁻⁶ M

In a separate experiment, the Mg(OH)₂ is precipitated by adding 0.10 mol of Mg(NO₃)₂ to 1.0 L of a 0.10 M NH₃ solution. What amount (in mol) of NH₄Cl must be added to this solution to just dissolve the precipitate? The pK_a of NH₄Cl is 9.24.

With $[Mg^{2+}(aq)] = 0.10$ M, dissolution will start to occur when:

$$[OH^{-}(aq)]^{2} \le \frac{K_{sp}}{[Mg^{2+}(aq)]} = \frac{(7.1 \times 10^{-12})}{(0.10)}$$
 so $[OH^{-}(aq)] \le 8.4 \times 10^{-6} \text{ M}$

This [OH⁻(aq)] corresponds to pOH = $-\log_{10}([OH⁻(aq)]) = -\log_{10}(8.4 \times 10^{-6}) = 5.1$. Using pH = 14.0 – pOH, pH = (14.0 – 5.1) = 8.9.

When NH_4Cl is added, the solution contains an acid (NH_4Cl) and its conjugate base (NH_3) . The solution contains an acid (NH_4Cl) and its conjugate base (NH_3) . The Henderson-Hasselbalch equation can be used to work out the required $[NH_4Cl]$ with $[NH_3] = 0.10$ M and pH = 8.9:

$$pH = pK_{a} + \log_{10}\left(\frac{[base]}{[acid]}\right) = 9.24 + \log_{10}\left(\frac{0.10}{[NH_{4}Cl]}\right) = 8.9$$
$$\left(\frac{0.10}{[NH_{4}Cl]}\right) = 10^{(8.9-9.24)} \text{ so } [NH_{4}Cl] = 0.2 \text{ M}$$

This molarity is for a 1.0 L solution so that 0.2 mol of NH₄Cl are required.

ANSWER: 0.2 mol

Marks • The solubility product constant of Fe(OH)₃ is 1×10^{-39} M⁴. What is the concentration of 4 $Fe^{3+}(aq)$ in equilibrium with $Fe(OH)_3$ at pH 7.0? As pH + pOH = 14.0 and $pOH = -log_{10}([OH^{-}(aq)], [OH^{-}(aq)] = 10^{-7.0}$. The dissolution reaction and solubility product are: $Fe(OH)_{3}(s) \iff Fe^{3+}(aq) + 3OH^{-}(aq) \qquad K_{sp} = [Fe^{3+}(aq)][OH^{-}(aq)]^{3}$ With $K_{sp} = 1 \times 10^{-39}$ and $[OH^{-}(aq)] = 10^{-7.0}$, $[\mathrm{Fe}^{3+}(\mathrm{aq})] = \frac{K_{\mathrm{sp}}}{[\mathrm{OH}^{-}(\mathrm{aq})]^{3}} = \frac{(1 \times 10^{-39})}{(10^{-7.0})^{3}} = 1 \times 10^{-18} \mathrm{M}$ ANSWER: 1 × 10⁻¹⁸ M To what value does the pH need to be increased to decrease the concentration of $Fe^{3+}(aq)$ to a single $Fe^{3+}(aq)$ ion per litre of solution? A single $Fe^{3+}(aq)$ ion corresponds to: number of moles = $\frac{\text{number of ions}}{\text{Avogadro's number}} = \frac{1}{6.022 \times 10^{23}} = 1.66 \times 10^{-24} \text{ mol}$ If this is in a litre of solution, $[Fe^{3+}(aq)] = 1.66 \times 10^{-24}$ M. As $K_{sp} = [Fe^{3+}(aq)][OH^{-}(aq)]^{3}$, $[OH^{-}(aq)]^{3} = \frac{K_{sp}}{[Fe^{3+}(aq)]} = \frac{(1 \times 10^{-39})}{(1.66 \times 10^{-24})} = 6 \times 10^{-16} \text{ M}^{3}$ $[OH^{-}(aq)] = 8 \times 10^{-6} M$ Thus, $pOH = -log_{10}([OH^{-}(aq)]) = -log_{10}(8 \times 10^{-6}) = 5$ and as pH = 14 - pOH, pH = 14 - 5 = 9ANSWER: 9

• Teeth are made from hydroxyapatite, Ca₅(PO₄)₃OH. Why does an acidic medium promote tooth decay and how can the decay be stopped using fluoridation of drinking water? Use chemical equations where appropriate.

Hydroxyapatite dissolves according to the equation:

$$Ca_{5}(PO_{4})_{3}OH(s) \implies 5Ca^{2+}(aq) + 3PO_{4}^{3-}(aq) + OH^{-}(aq)$$

This equilibrium lies far to the left so that hydroxyaptite does not dissolve to any significant degree. However, the addition of H_3O^+ (i.e. an acidic medium) will decrease [OH⁻(aq)] and push the reaction to the right (Le Chatelier's principle).

Fluoridation of water promotes the replacement of OH^- with F^- to form $Ca_5(PO_4)_3F(s)$. This compound is much less water soluble than $Ca_5(PO_4)_3OH$:

 $Ca_5(PO_4)_3F(s) \iff 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + F^{-}(aq)$

 F^- is a weaker base than OH^- so this equilibrium is less affected by the addition of H_3O^+ . As the enamel is less soluble, this promotes less tooth decay.