- Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3}, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9}. **2**

The Fe^{3+} ion is much smaller and has a much higher charge density than the Fe^{2+} ion. This results in a stronger Fe–O bond and a weakening of the O–H bonds. The high charge density on the Fe^{3+} ion pulls electron density from the attached OH_2 ligands. This leads to the release of H^+(aq).

As the O–H bonds are weaker, it is more acidic: it has a much *greater* value for K_a.

Marks

- Write a balanced chemical equation representing the dissolution of $FeCO_3$ in water at pH 7. **4**

$FeCO_3(s) \rightarrow Fe^{2+}(aq) + CO_3^{2-}(aq)$

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, $K_{sp} = [Fe^{2+}(aq)][CO_3^{2-}(aq)]$. If s mol of $FeCO_3$ dissolves in 1.0 L, $[Fe^{2+}(aq)] = [CO_3^{2-}(aq)] = s$ M. Hence:

$$K_{sp} = [Fe^{2+}(aq)][CO_3^{2-}(aq)] = (s)(s) = s^2 = 2.1 \times 10^{-11} \text{ or } s = 4.6 \times 10^{-6} \text{ M}$$

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

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

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

Answer: **5.3×10^{-4} g L^{-1}**

- 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 $Fe^{3+}(aq)$ in the ocean at this pH? The K_{sp} of $Fe(OH)_3$ is 1×10^{-39}. **4**

As pH + pOH = 14.00, pOH = 14.00 – 8.22 = 5.78.

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

$Fe(OH)_3$ dissolves according to the equilibrium:

$$Fe(OH)_3 \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq) \quad \text{with } K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3.$$

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

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

Answer: **2×10^{-22} M**

ANSWER CONTINUES ON THE NEXT PAGE

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

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

$$2OH^-(aq) + CO_2(aq) \rightarrow CO_3^{2-}(aq) + H_2O$$

From Le Chatelier's principle, the decrease in [OH^-(aq)] will result in an increase in [Fe^{3+}(aq)].

Equivalently, if [OH^-(aq)] is decreased, [Fe^{3+}(aq) must increase as K_{sp} is a constant.