Teeth are made from hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. 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:

$$\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{OH}^-(aq)$$

This equilibrium lies far to the left so that hydroxyapatite does not dissolve to any significant degree. However, the addition of $\text{H}_3\text{O}^+$ (i.e. an acidic medium) will decrease $[\text{OH}^-(aq)]$ and push the reaction to the right (Le Chatelier's principle).

Fluoridation of water promotes the replacement of $\text{OH}^-$ with $\text{F}^-$ to form $\text{Ca}_5(\text{PO}_4)_3\text{F}(s)$. This compound is much less water soluble than $\text{Ca}_5(\text{PO}_4)_3\text{OH}$:

$$\text{Ca}_5(\text{PO}_4)_3\text{F}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4^{3-}(aq) + \text{F}^-(aq)$$

$\text{F}^-$ is a weaker base than $\text{OH}^-$ so this equilibrium is less affected by the addition of $\text{H}_3\text{O}^+$. As the enamel is less soluble, this promotes less tooth decay.
Solution A consists of a 0.15 M aqueous solution of nitrous acid (HNO₂) at 25 °C. Calculate the pH of Solution A. The pKₐ of HNO₂ is 3.15.

<table>
<thead>
<tr>
<th></th>
<th>HNO₂(aq)</th>
<th>H₂O(l)</th>
<th>H₃O⁺(aq)</th>
<th>NO₂⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.15</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.15 – x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.15 - x}$$

As $K_a = 10^{-3.15}$ is very small, $0.15 - x \sim 0.15$ and hence:

$$x^2 = 0.15 \times 10^{-3.15} \quad \text{or} \quad x = 0.0103 \text{ M} = [H_3O^+(aq)]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+(aq)] = -\log_{10}[0.0103] = 1.99$$

ANSWER: pH = 1.99

ANSWER CONTINUES ON THE NEXT PAGE
At 25 °C, 1.00 L of Solution B consists of 13.8 g of sodium nitrite (NaNO₂) dissolved in water. Calculate the pH of Solution B.

The formula mass of NaNO₂ is (22.99 Na) + 14.01 (N) + 2 × 16.00 (O) = 69. 13.8 g therefore corresponds to:

\[ \text{amount of NaNO}_2 = \frac{\text{mass}}{\text{formula mass}} = \frac{13.8}{69.0} = 0.200 \text{ mol} \]

A 1.00 L solution containing this amount has a molarity of 0.200 M. The nitrite ion acts as a base and [OH⁻(aq)] must be calculated from the equilibrium:

\[ \text{NO}_2^- (aq) + H_2O(l) \rightleftharpoons OH^- (aq) + HNO_2(aq) \]

<table>
<thead>
<tr>
<th></th>
<th>NO₂⁻(aq)</th>
<th>H₂O(l)</th>
<th>OH⁻(aq)</th>
<th>HNO₂(aq)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-y</td>
<td>negligible</td>
<td>+y</td>
<td>+y</td>
</tr>
<tr>
<td>final</td>
<td>0.200 – y</td>
<td>large</td>
<td>y</td>
<td>y</td>
</tr>
</tbody>
</table>

The equilibrium constant \( K_b \) is given by:

\[ K_a = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{y^2}{0.200 - y} \]

In aqueous solution, \( pK_a + pK_b = 14.00 \). Hence \( pK_b = (14.00 - 3.15) = 10.85 \) and as \( K_b = 10^{-10.85} \) is very small, \( 0.200 - y \approx 0.200 \) and hence:

\[ y^2 = 0.200 \times 10^{-10.85} \text{ or } y = 1.68 \times 10^{-6} \text{ M} = [\text{OH}^-(aq)] \]

Hence, the pOH is given by:

\[ \text{pOH} = -\log_{10}[\text{OH}^-(aq)] = -\log_{10}[1.68 \times 10^{-6}] = 5.77 \]

As \( \text{pH} + \text{pOH} = 14 \), \( \text{pH} = 8.23 \)

**Answer:** \( \text{pH} = 8.23 \)

**Answer continues on the next page**
Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C. Calculate the pH of the final solution.

This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used. As [acid] = [HNO₂] = 0.15 M and [base] = [NO₂⁻] = 0.200 M:

\[
pH = pK_a + \log_{10} \left( \frac{[base]}{[acid]} \right) = 3.15 + \log_{10} \left( \frac{0.200}{0.15} \right) = 3.27
\]

ANSWER: pH = 3.27

If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration? The acid, HNO₂
Calculate the pH of a solution that is prepared by mixing 500 mL of 1.0 M \( \text{NH}_3 \) with 500 mL of 2.0 M \( \text{NH}_4\text{Cl} \). The \( pK_b \) of \( \text{NH}_3 \) is 4.76.

The solution contains an acid (\( \text{NH}_4\text{Cl} \)) and its conjugate base (\( \text{NH}_3 \)) so the Henderson-Hasselbalch equation can be used.

In aqueous solution, \( pK_a + pK_b = 14.00 \). Hence, \( pK_a = 14.00 – 4.76 = 9.24 \).

Before mixing the 500 mL solutions, \([\text{acid}] = [\text{NH}_4\text{Cl}] = 2.0 \text{ M} \) and \([\text{base}] = [\text{NH}_3] = 1.0 \text{ M} \). Mixing produces a 1.0 L solution which halves each concentration, \([\text{NH}_4\text{Cl}] = 1.0 \text{ M} \) and \([\text{NH}_3] = 0.5 \text{ M} \). (As equal volumes of each are used and the Henderson-Hasselbach equation uses the ratio, this step is unnecessary).

Using the Henderson-Hasselbalch equation:

\[
\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 9.24 + \log_{10} \left( \frac{0.5}{1.0} \right) = 8.9
\]

**ANSWER:** \( \text{pH} = 8.9 \)