Regulation of our blood’s pH value is of vital importance for our health. In a healthy person the blood pH does not vary by more than 0.2 from the average 7.4. How does our body regulate the pH of blood?

Blood maintains a constant pH by means of a $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer. It resists any change in pH because any excess $\text{H}^+$ or $\text{OH}^-$ is consumed as follows:

excess acid: $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$

excess base: $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$

During exercise, $\text{CO}_2$ is produced at a rapid rate in muscle tissue. What effect does this have on the pH of blood? Why?

The buffer is an equilibrium system:

$$\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3$$

As more $\text{CO}_2$ is produced, it dissolves in the blood to increase the concentration of $\text{H}_2\text{CO}_3$. This in turn pushes the above equilibrium to the left and the $[\text{H}^+]$ increases. The pH will therefore go down, but only slightly as the buffer system is highly effective.

Hyperventilation (rapid and deep breathing) can occur during intense exertion. What effect does hyperventilation have on the pH of blood? Why?

Hyperventilation results in a decrease in the amount of $\text{CO}_2$ in the blood. This pushes the $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ equilibrium to the left which in turn pushes the $\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3$ equilibrium to the right to produce more $\text{H}_2\text{CO}_3$. The net effect is thus to lower $[\text{H}^+]$ and cause a small increase in pH. (The standard treatment for hyperventilation is to get the patient to breath into a paper bag and rebreathe the $\text{CO}_2$ they have exhaled.)
• Find the concentration of $H_3O^+$ in a 0.60 M aqueous solution of nitrous acid. The acid dissociation constant of HNO$_2$ is $K_a = 7.1 \times 10^{-4}$ M.

As nitrous acid is a weak acid, $[H_3O^+]$ must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>HNO$_2$</th>
<th>H$_2$O</th>
<th>$\rightleftharpoons$</th>
<th>H$_3$O$^+$</th>
<th>NO$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.60</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>$-x$</td>
<td>negligible</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.60 – $x$</td>
<td>large</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.60-x} = 7.1 \times 10^{-4} \text{ M}$$

As $K_a$ is very small, $0.60 – x \sim 0.60$ and hence:

$$x^2 = 0.60 \times 7.1 \times 10^{-4} \quad \text{or} \quad x = 0.021 \text{ M} = [H_3O^+]$$

Answer: 0.021 M

• An aqueous solution of a weak acid has $[H_3O^+] = 2.54 \times 10^{-4}$ M. Find the pH and pOH of the solution.

$$\text{pH} = –\log_{10}[H_3O^+] = –\log_{10}[2.54 \times 10^{-4}] = 3.60$$
$$\text{pH} + \text{pOH} = 14.00 \quad \text{or} \quad \text{pOH} = 14.00 – \text{pH} = 14.00 – 3.60 = 10.40$$

$\text{pH} = 3.6$ \hspace{2cm} $\text{pOH} = 10.40$
Calculate the pH of a 0.200 M solution of acetic acid, CH₃COOH, at 25 ºC. (The pKₐ of acetic acid is 4.76).

As acetic acid is a weak acid, [H₃O⁺] must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH</th>
<th>H₂O</th>
<th>CH₃COO⁻</th>
<th>H₃O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.200</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>0.200 - x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:  

\[ K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.2 - x} \]

As pKₐ = 4.76 = -\log_{10} K_a so \( K_a = 10^{-4.76} \). As \( K_a \) is very small, \( 0.200 - x \sim 0.200 \) and hence:

\[ x^2 = 0.200 \times 10^{-4.76} \quad \text{or} \quad x = 0.0019 \text{ M} = [H_3O^+] \]

Hence, the pH is given by:

\[ \text{pH} = -\log_{10}[H_3O^+] = -\log_{10}[0.0019] = 2.73 \]

\[ \text{pH} = 2.73 \]

Solid sodium acetate, NaCH₃CO₂, (0.15 mol) was dissolved in 0.500 L of 0.200 M acetic acid and the volume made up to 750 mL with water. What is the pH of the resulting solution?

The solution contains a weak acid (acetic acid) and its conjugate base (acetate). 0.15 mol of acetate is present in 750 mL so its concentration is:

\[ [\text{base}] = (0.15 \text{ mol}) / (0.750 \text{ L}) = 0.20 \text{ M} \]

500 mL of 0.200 M acid contains \((0.5 \text{ L}) \times (0.200 \text{ M}) = 0.100 \text{ mol} \). The concentration of the acid in 750 mL is therefore:

\[ [\text{acid}] = (0.100 \text{ mol}) / (0.750 \text{ L}) = 0.133 \text{ M} \]

The Henderson-Hasselbalch equation can be used for this buffer:

\[ \text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 4.76 + \log_{10} \left( \frac{0.20}{0.133} \right) = 4.94 \]

\[ \text{pH} = 4.94 \]

ANSWER CONTINUES ON THE NEXT PAGE
How much more NaCH$_3$CO$_2$ needs to be dissolved in the above solution to give a final pH of 5.00?

A pH of 5.00 will be obtained when:

$$\text{pH} = 4.76 + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 5.00 \text{ or } \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 0.24$$

Hence,

$$\left( \frac{[\text{base}]}{[\text{acid}]} \right)^{10^{0.24}} = 1.74 \text{ or } [\text{base}] = 1.74 \times [\text{acid}] = 1.74 \times 0.133 = 0.232 \text{ M}$$

The number of moles of base in 750 mL is therefore $(0.232 \text{ M}) \times (0.750 \text{ L}) = 0.174 \text{ mol}$. 

As 0.15 mol was added originally, an additional $(0.17 - 0.15) = 0.02 \text{ mol}$ is required.

Answer: 0.02 mol
Solution A consists of a 0.15 M aqueous solution of HF at 25 °C. Calculate the pH of Solution A. The pK_a of HF is 3.17.

As HF is a weak acid, [H_3O^+] must be calculated:

<table>
<thead>
<tr>
<th>Initial</th>
<th>HF</th>
<th>H_2O</th>
<th>H_3O^+</th>
<th>F^-</th>
</tr>
</thead>
<tbody>
<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:  

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

As pK_a = 3.17 = –log_{10}K_a so K_a = 10^{-3.17}. As K_a is very small, 0.15 – x ~ 0.15 and hence:

$$x^2 = 0.15 \times 10^{-3.17} \quad \text{or} \quad x = 0.00101 \text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[0.00102] = 2.00$$

pH = 2.00

ANSWER CONTINUES ON THE NEXT PAGE
At 25 °C, 1.00 L of Solution B consists of 11.62 g of KF dissolved in water. Calculate the pH of Solution B.

The molar mass of KF is 39.10 (K) + 19.00 (F) = 58.1. Hence, 11.62 g corresponds to \( \frac{11.62 \text{g}}{58.1 \text{g mol}^{-1}} = 0.2000 \text{ mol} \). When this number of moles dissolves in 1.00 L, the concentration of the solution is 0.20 M. As \( \text{F}^- \) is a weak acid, \([\text{H}_3\text{O}^+]\) must be calculated:

<p>| | | | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>F^-</td>
<td>H_2O</td>
<td>-&gt;</td>
<td>OH^-</td>
<td>HF</td>
</tr>
<tr>
<td>initial</td>
<td>0.20</td>
<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>0.20 - y</td>
<td>large</td>
<td>y</td>
<td>y</td>
</tr>
</tbody>
</table>

The equilibrium constant \( K_b \) is given by: \( K_b = \frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} = \frac{y^2}{0.20 - y} \)

\( \text{F}^- \) is the conjugate base of HF so \( pK_a + pK_b = 14.00 \) and hence:

\( pK_b = 14.00 - 3.17 = 10.83. \)

As \( K_b \) is very small, \( 0.20 - y \sim 0.20 \) and hence:

\( y^2 = 0.20 \times 10^{-10.83} \) or \( y = 1.72 \times 10^{-6} \text{ M} = [\text{OH}^-]. \)

Hence, \( p\text{OH} \) is given by \( p\text{OH} = -\log_{10}[\text{OH}^-] = -\log_{10}[1.72 \times 10^{-6}] = 5.76 \)

As \( p\text{H} + p\text{OH} = 14.00, p\text{H} = 14.00 - 5.76 = 8.24 \)

\[ \text{pH} = 8.24 \]

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.

The solution contains a weak acid, HF, and its conjugate base, \( \text{F}^- \): it is a buffer and so the Henderson-Hasselbalch equation can be used:

\[ \text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 3.17 + \log_{10} \left( \frac{0.20}{0.15} \right) = 3.29 \]

\[ \text{pH} = 3.29 \]

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 solution would you need to increase in concentration? To lower the pH, more acid is needed: HF is added.