Trichloroacetic acid, CCl$_3$COOH, a corrosive acid used to precipitate proteins, has a $K_a$ of 0.16 M. What is the pH of a 0.050 M solution of trichloroacetic acid?

Hint: If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

The reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>CCl$_3$COOH</th>
<th>H$_2$O</th>
<th>$\rightleftharpoons$</th>
<th>H$_3$O$^+$</th>
<th>CCl$_3$COO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.050</td>
<td>large</td>
<td>0</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>0.050 $-x$</td>
<td>large</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[H_3O^+(aq)][CCl_3COO^-(aq)]}{[CCl_3COOH(aq)]} = \frac{x^2}{0.050 - x} = 0.16$$

$K_a$ is not sufficiently small that any approximation to this equation can be made. Hence, the quadratic expression must be solved:

$$x^2 = (0.16 \times 0.050) - 0.16x \text{ or } x^2 + 0.16x - 0.0080$$

With $a = 1$, $b = +0.16$ and $c = -0.0080$, the roots are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.16 \pm \sqrt{(0.16)^2 - (4 \times 1 \times -0.0080)}}{2(2 \times 1)} = \frac{-0.16 \pm 0.24}{2}$$

Only the positive root has physical significance so $x = \frac{-0.16 + 0.24}{2} = 0.04$

As $[H_3O^+(aq)] = x = 0.04$ M and pH = $-\log_{10}([H_3O^+(aq)])$:

$$\text{pH} = -\log_{10}(0.04) = 1.4$$

Answer: pH = 1.4
The H$_2$PO$_4^-$ and HPO$_4^{2-}$ ions play a major role in maintaining the intracellular pH balance. Write balanced equations to show how a solution containing these ions can act as a buffer.

The presence of H$_2$PO$_4^-$ (aq) means that the solution can remove OH$^-$ (aq):

\[
\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l)
\]

The presence of HPO$_4^{2-}$ (aq) means that the solution can remove H$^+$ (aq):

\[
\text{HPO}_4^{2-}(aq) + \text{H}^+(aq) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq)
\]

For phosphoric acid, $K_{a1} = 7.1 \times 10^{-3}$ M, $K_{a2} = 6.3 \times 10^{-8}$ M, $K_{a3} = 4.2 \times 10^{-13}$ M.

At what pH would the H$_2$PO$_4^-$ / HPO$_4^{2-}$ buffer system be most effective? Why?

Buffers are most effective when [acid] = [base] at which point pH = pK$_a$. For this system, this requires [H$_2$PO$_4^-$(aq)] = [HPO$_4^{2-}$(aq)]. This acid / base equilibrium corresponds to $K_{a2}$:

\[
\text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}^+(aq)
\]

Thus, pH = pK$_{a2}$ = -log$_{10}(6.3 \times 10^{-8}) = 7.20$

Calculate the ratio of H$_2$PO$_4^-$ / HPO$_4^{2-}$ needed to give a solution buffered to a pH of 7.35.

Using the Henderson-Hasselbalch equation:

\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{or} \quad \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{pK}_a
\]

Thus:

\[
\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{pK}_{a2} = 7.35 - 7.20 = 0.15
\]

\[
\left( \frac{[\text{base}]}{[\text{acid}]} \right) = 10^{0.15} = 1.4 \quad \text{or} \quad \left( \frac{[\text{acid}]}{[\text{base}]} \right) = \frac{1}{1.4} = 0.71
\]
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.

The reaction table is:

<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>0</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:

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

$K_a$ is very small compared to the initial concentration of HNO$_2$ so that $0.60 - x \sim 0.60$ and so:

$$x^2 \sim (7.1 \times 10^{-4}) \times (0.60) \text{ so } x = [H_3O^+(aq)] = x = 0.021 \text{ M}$$

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.

Using pH = $-\log_{10}([H_3O^+(aq)])$ and pH + pOH = 14.00:

$$\text{pH} = -\log_{10}(2.54 \times 10^{-4}) = 3.60$$

$$\text{pOH} = 14.00 - 3.60 = 10.40$$

pH = 3.60

pOH = 10.40

Ammonia, NH$_3$, is a Brønsted-Lowry base and a Lewis base, but not an Arrhenius base. Why?

A Brønsted-Lowry base is a proton (H$^+$) acceptor: $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$

A Lewis base is a species that can donate a lone pair: $\cdot\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$

An Arrhenius base is one that contains OH$^-$ ions that are released on dissolution in water. Ammonia generates OH$^-$ ions in its reaction with water but does not contain them in its formula and hence it is not an Arrhenius base.
Triethylamine, N(CH₂CH₃)₃, is a weak base with $K_b = 5.2 \times 10^{-4}$ M. A 20.00 mL solution of 0.100 M triethylamine was titrated with 0.100 M HCl. Calculate the pH of the titration solution after the addition of:

### a) 5.00 mL HCl solution

The neutralization reaction is:

$$\text{Et}_3\text{N}(aq) + \text{HCl}(aq) \rightarrow \text{Et}_3\text{NH}^+(aq) + \text{Cl}^-(aq)$$

The number of moles of Et₃N and HCl are:

$$n(\text{Et}_3\text{N}) = \text{volume} \times \text{concentration} = 0.02000 \text{ L} \times 0.100 \text{ M} = 0.00200 \text{ mol}$$

$$n(\text{HCl}) = \text{volume} \times \text{concentration} = 0.00500 \text{ L} \times 0.100 \text{ M} = 0.000500 \text{ mol}$$

After the neutralization reaction, 0.000500 moles of Et₃NH⁺ will be made and

$$(0.00200 - 0.000500) = 0.001500 \text{ moles of Et}_3\text{N will be left. The total volume of the solution will now be } 20.00 + 5.00 = 25.00 \text{ mL. The concentrations will be:}$$

$$[\text{Et}_3\text{N}] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.001500}{0.02500} = 0.0600 \text{ M}$$

$$[\text{Et}_3\text{NH}^+] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.000500}{0.02500} = 0.0200 \text{ M}$$

The pH of the solution depends on $[\text{H}_3\text{O}^+(aq)]$ which itself depends on the equilibrium between Et₃N(aq) and Et₃NH⁺(aq):

$$\text{Et}_3\text{N}(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{Et}_3\text{NH}^+(aq) + \text{OH}^-(aq)$$

$$K_b = \frac{[\text{Et}_3\text{NH}^+(aq)][\text{OH}^-(aq)]}{[\text{Et}_3\text{N}(aq)]} = \frac{(0.0200) \times [\text{OH}^-(aq)]}{(0.0600)} = 5.2 \times 10^{-4}$$

Hence, $[\text{OH}^-(aq)] = 0.0016 \text{ M}$

As $K_w = [\text{H}_3\text{O}^+(aq)][\text{OH}^-(aq)] = 10^{-14}$, hence:

$$[\text{H}_3\text{O}^+(aq)] = \frac{(10^{-14})}{(0.0016)} = 6.4 \times 10^{-12} \text{ M and}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+(aq)]) = -\log_{10}(6.4 \times 10^{-12}) = 11.19$$

$$\text{pH} = 11.19$$

ANSWER CONTINUES ON THE NEXT PAGE
b) 20.10 mL HCl solution

20.00 mL of the added HCl solution will simply neutralize all of the Et₃N(aq) present. The excess, \((20.10 - 20.00) = 0.10 \text{ mL}\), HCl will produce \([\text{H}_3\text{O}^+\text{(aq)}]\).

As the HCl solution is 0.100 M so the number of moles of \([\text{H}_3\text{O}^+\text{(aq)}]\) in this volume is:

\[
n(\text{H}_3\text{O}^+\text{(aq)}) = \text{volume} \times \text{concentration} = \frac{0.10}{1000} \text{ L} \times 0.100 \text{ M} = 1.00 \times 10^{-5} \text{ M}
\]

This is dissolved in a total volume of \((20.00 + 20.10) = 40.10 \text{ mL}\) so,

\[
[\text{H}_3\text{O}^+\text{(aq)}] = \frac{\text{number of moles}}{\text{volume}} = \frac{1.00 \times 10^{-5}}{40.10/1000} = 2.49 \times 10^{-4} \text{ M}
\]

\[
\text{pH} = \log_{10}(2.49 \times 10^{-4}) = 3.60
\]

- Tris(hydroxymethyl)aminomethane, commonly called TRIS, is a weak base with \(K_b = 1.19 \times 10^{-6}\) M. It is often used in buffers for biochemical research. It reacts with water according to the following equation.

\[
(\text{HOCH}_2\text{CNH}_2\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HOCH}_2\text{CNH}_3^+\text{(aq)} + \text{OH}^-\text{(aq)}
\]

At what pH does TRIS show its maximum buffering ability?

For this buffer, the Henderson-Hasselbalch equation can be used:

\[
\text{pH} = \text{p}K_a + \log_{10}\left(\frac{\text{[base]}}{\text{[acid]}}\right)
\]

The maximum buffering ability occurs when \([\text{base}] = [\text{acid}]\) when \(\text{pH} = \text{p}K_a\).

\(K_a\) and \(K_b\) are related as \(K_a \times K_b = K_w = 10^{-14.00}\).

Hence:

\[
K_a = \frac{10^{-14.00}}{1.19 \times 10^{-6}} = 8.40 \times 10^{-9}
\]

\[
\text{pH} = \text{p}K_a = -\log_{10}(8.40 \times 10^{-9}) = 8.08
\]

\[
\text{pH} = 8.08
\]
What is the TRIS/TRIS-H⁺ ratio in a buffer of pH 7.40?

Using the Henderson-Hasselbalch equation:

\[
\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{or} \quad \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{p}K_a
\]

\[
\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = (7.40) - (8.08) = -0.68
\]

\[
\left( \frac{[\text{base}]}{[\text{acid}]} \right) = 10^{-0.68} = 0.21
\]

Answer: 0.21