The auto-ionization of water is unfavorable but happens to a small degree since at any temperature a few molecules will have enough energy to dissociate.

\[ H_2O \rightleftharpoons H^+ + OH^- \]  
\[ K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at only one temperature} \]

In pure water at \( 25^\circ C \), \( [H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M} \)

\[ pH = -\log_{10} [H^+] = 7.00 \]

\[ pH = 7 \text{ means neutral only at this temperature} \]

\[ \text{HA} \rightleftharpoons A^- + H^+ \]  
\( \text{conjugate} \)

\( [H^+] [A^-] = K_a \)

\[ \text{NH}_3 + H_2O \rightleftharpoons OH^- + \text{NH}_4^+ \]

\( B + H_2O \rightleftharpoons OH^- + HB^0 \)  
\( \text{conjugate} \)

\[ [OH^-] [HB] = K_b \]

If \( A^- = B \)

\[ K_a \cdot K_b = \frac{[H^+][A^-]}{[HA]} = \frac{[OH^-][HB]}{[B]} = K_w \]

An acid's strength is inversely proportional to its conjugate base's strength.

\[ \text{Strong acid} \]

<table>
<thead>
<tr>
<th>Concentration</th>
<th>pH</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>X 0</td>
<td>( \times )</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td></td>
<td>( \times )</td>
</tr>
<tr>
<td>0.001 M HCl</td>
<td>2</td>
<td>( \times )</td>
</tr>
</tbody>
</table>

When solutions are highly concentrated, interactions between solute particles can cause deviation from predicted solution behavior → activity.

\[ \text{Strong acid} \]

Heavy spontaneous dissociation → large \( K_a \)  
→ small \( pK_a \)

\( pK_a (\text{HCl}) < 0 \)
Given 1 M acetic acid (and ignoring activity), what is the pH? 
\[ pK_a = 4.76, \quad K_a = 1.76 \times 10^{-5} \]

\[ \begin{align*}
\text{HA} & \quad \text{H}^+ & \quad \text{A}^- & \quad K_a = \frac{(x)(x)}{1-x} = 1.76 \times 10^{-5} \\
\text{Initial} & \quad 1.00 & \quad \rightarrow & \quad 0 & \quad x^2 = 1.76 \times 10^{-5} \\
\text{Change} & \quad -x & \quad +x & \quad +x & \quad x = 4.19 \times 10^{-3} \quad \Rightarrow \quad \text{pH} = 2.38 \\
\text{End} & \quad 1-x \\
\end{align*} \]

If \( x \ll 1 \), it \((x)\) can be ignored.

Given 0.500 M acetic acid + 0.500 M sodium acetate, what is the pH?

\[ \begin{align*}
\text{HA} & \quad \text{H}^+ & \quad \text{A}^- & \quad K_a = 1.76 \times 10^{-5} \\
\text{I} & \quad 0.50 & \quad "\text{O}" & \quad 0.50 & \quad = \frac{(5+x)(x)}{15-x} \\
\text{C} & \quad -x & \quad x & \quad x & \quad x = 0.5 \times 10^{-5} \\
\text{E} & \quad 0.5-x & \quad x & \quad 0.5+x & \quad \text{If } x \ll 2.5 \\
\end{align*} \]

\( x = 1.76 \times 10^{-5} \), \( pH = 4.76 = pK_a \quad \Rightarrow \quad \frac{5(x)}{15} = x \)

*If \( x \) is not small compared to 15, this simplification is not possible.

*When an acid + a conjugate are added together, a small shift in their concentrations will occur.

But, if the acid is weak, that shift can often be ignored.

\[ pK_a = \frac{[\text{CH}_3\text{CO}_2^\text{−}][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} \quad \Rightarrow \quad -\log_{10}(K_a) = -\log_{10}\left[\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{H}^+][\text{CH}_3\text{CO}_2\text{H}]}\right] \]

\[ pK_a = -\log_{10}[\text{H}^+] + (-\log_{10}\left[\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{H}^+]}ight]) \]

\[ pK_a = pH - \log_{10}\left(\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{H}^+]}ight) \]

\[ pH = pK_a + \log_{10}\left(\frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{H}^+]}ight) \]

Henderson-Hasselbalch eq.
Titration

\[ \text{H}_2\text{O}^- + \text{NaOH} \rightarrow \text{Na}_2\text{O}^+ + \text{H}_2\text{O} \]

unknown concentration

0.1000M

Indicator - The indicator for a titration is chosen such that the pKa of the indicator is the same as the expected pH of the neutralized sol'n.

Neutral \equiv Neutralized

If a weak acid and/or neutralized, weak base are used in titration, the moles of \([\text{H}^+]/[\text{OH}^-]\) would not be the same as the moles of acid/base.

If incompletely dissociated would occur.

Acetic acid + sodium hydroxide

weak acid \rightarrow strong base

Once acetic acid is fully neutralized by sodium hydroxide, a salt is produced (sodium acetate). This product is the result of the forced complete dissociation of a weak acid. Once formed, the salt will thus want to re-establish equilibrium with the acid, so it will react with water, forming hydroxide, resulting in a basic solution.

Equivalence point - When equal moles of acid + base have been reacted.

Endpoint - The visual observation that a titration is complete (color change).
As titrant is added linearly, pH changes exponentially.

Volume of titrant

@ half equivalence, $\ce{CH_3COOH} \rightleftharpoons \ce{CH_3COO^-} + \ce{H^+}$

$\text{p}K_a = \frac{[\ce{H^+}][\ce{CH_3COO^-}]}{[\ce{CH_3COOH}]} \Rightarrow K_a = [\ce{H^+}] \Rightarrow \text{p}K_a = \text{pH}$

@ equivalence: $\text{M}_{\text{acid}} \times V_{\text{acid}} = \text{M}_{\text{base}} \times V_{\text{base}}$

unknown measured

Calculated (standardized)