Lecture 14
Acid/base equilibria.
pKₐ and pH
Acid strength : the acid dissociation constant $K_A$.

Chemistry 3 Section 6.2, pp.268-270.

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.
- The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.
- The question is how small is small?
- We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant $K_A$.

$K_A$ values vary over a wide range so it is best to use a log scale.

$\text{p}K_A = -\log_{10} K_A$

The Meaning of $K_A$, the Acid Dissociation Constant

For the ionization of an acid, HA:

\[
K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}
\]

Therefore:

\[
K_A = K_C[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}
\]

The stronger the acid, the higher the $[H_3O^+]$ at equilibrium, and the larger the $K_A$:

Stronger acid $\rightarrow$ higher $[H_3O^+]$ $\rightarrow$ larger $K_A$

For a weak acid with a relative high $K_A (~10^{-2})$, a 1 M solution has ~10% of the HA molecules dissociated.
For a weak acid with a moderate $K_A (~10^{-5})$, a 1 M solution has ~ 0.3% of the HA molecules dissociated.
For a weak acid with a relatively low $K_A (~10^{-10})$, a 1 M solution has ~ 0.001% of the HA molecules dissociated.
Acid strengths and $K_a$ value.

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure$^*$</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine acid (HIO$_3$)</td>
<td></td>
<td>$1.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>Chlorous acid (HClO$_2$)</td>
<td></td>
<td>$1.12 \times 10^{-3}$</td>
</tr>
<tr>
<td>Nitrous acid (HNO$_2$)</td>
<td></td>
<td>$7.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td></td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>Formic acid (HCOOH)</td>
<td></td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Benzoic acid (C$_6$H$_5$COOH)</td>
<td></td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Acetic acid (CH$_3$COOH)</td>
<td></td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Propionic acid (CH$_3$CH$_2$COOH)</td>
<td></td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hypochlorous acid (HClO)</td>
<td></td>
<td>$2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hydrobromic acid (HBr)</td>
<td></td>
<td>$2.3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hydrocyanic acid (HCN)</td>
<td></td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>Phosphoric acid (H$_3$PO$_4$)</td>
<td></td>
<td>$1.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>Hydrofluoric acid (HF)</td>
<td></td>
<td>$2.3 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

*Bold type indicates the coordinate proton; structures have been formal charge.

---

**Table 6.2** Acidic constants ($K_a$) and values of $pK_a$ for some common acids at 298K

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$ (mol/l) $pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Perchloric acid [chloric(VII) acid]</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Hydrobromic acid</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>$6.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>$2.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>Chloric acid [chloric(III) acid]</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>$6.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>$3.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Methanoic acid</td>
<td>$1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ethanoic acid</td>
<td>$6.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$6.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Propanoic acid [chloric(III) acid]</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>$4.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Hydrobromic acid</td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>Phenol</td>
<td>$1.6 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
The Relationship Between $K_a$ and $pK_a$

$$pK_A = -\log_{10} K_A$$

<table>
<thead>
<tr>
<th>Acid Name (Formula)</th>
<th>$K_a$ at 298 K</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfate ion (HSO$_4^-$)</td>
<td>$1.02 \times 10^{-2}$</td>
<td>1.991</td>
</tr>
<tr>
<td>Nitrous acid (HNO$_2$)</td>
<td>$7.1 \times 10^{-4}$</td>
<td>3.15</td>
</tr>
<tr>
<td>Acetic acid (CH$_3$COOH)</td>
<td>$1.8 \times 10^{-5}$</td>
<td>4.74</td>
</tr>
<tr>
<td>Hypobromous acid (HBrO)</td>
<td>$2.3 \times 10^{-9}$</td>
<td>8.64</td>
</tr>
<tr>
<td>Phenol (C$_6$H$_5$OH)</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
</tbody>
</table>

When $K_a$ is small, $pK_a$ is large and the acid does not dissociate in solution to a large extent. A change in 1 $pK_a$ unit implies a 10-fold change in $K_a$ value and hence acid strength.

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**$K_a$ and $pK_a$**

Table 10.3 The Relationship Between $K_a$ and $pK_a$

<table>
<thead>
<tr>
<th>Acid Name (Formula)</th>
<th>$K_a$ at 25°C</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfate ion (HSO$_4^-$)</td>
<td>$1.02 \times 10^{-2}$</td>
<td>1.991</td>
</tr>
<tr>
<td>Nitrous acid (HNO$_2$)</td>
<td>$7.1 \times 10^{-4}$</td>
<td>3.15</td>
</tr>
<tr>
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<tr>
<td>Hypobromous acid (HBrO)</td>
<td>$2.3 \times 10^{-9}$</td>
<td>8.64</td>
</tr>
<tr>
<td>Phenol (C$_6$H$_5$OH)</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
</tbody>
</table>

**Acid Strength decreases**

$$pK_A = -\log_{10} K_A$$
**pKₐ calculation**

\[ K_a = \frac{[\text{CH}_3\text{CO}_2^-]\text{[H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5} \]

\[ pK_a = -\log(1.8 \times 10^{-5}) = 4.74 \]

**Weak acids**

- lactic acid \( \text{CH}_3\text{CH(OH)}\text{CO}_2\text{H} \)
- glycine \( \text{H}_2\text{NCH}_2\text{CO}_2\text{H} \)
**Acid-Base Properties of Water**

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

*autoionization* of water

\[ \text{H}_3\text{O}^+ + \text{OH}^- \]

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

**Autoionization of Water**

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

\[ K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \]

The ion-product for water, \( K_w \):

\[ K_c[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at 298K)} \]

For pure water the concentration of hydroxyl and hydronium ions must be equal:

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M (at 25°C)} \]

The molarity of pure water is:

\[ \frac{1000 \text{ g/L}}{18.02 \text{ g/mol}} = 55.5 \text{ M} \]
The Ion Product of Water

\[ \text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (aq) + \text{OH}^- (aq) \quad K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad [\text{H}_2\text{O}] = \text{constant} \]

\[ K_c[\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-] \]

The ion-product constant \((K_w)\) is the product of the molar concentrations of \(\text{H}^+\) and \(\text{OH}^-\) ions at a particular temperature.

\textbf{Solution Is}

\[
\begin{align*}
\text{At } 25^\circ \text{C} \\
K_w &= [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \\
\text{[H}^+] &= [\text{OH}^-] & \text{neutral} \\
\text{[H}^+] &> [\text{OH}^-] & \text{acidic} \\
\text{[H}^+] &< [\text{OH}^-] & \text{basic}
\end{align*}
\]

\begin{table}
\textbf{Table 6.3.} The effect of temperature on \(K_w\) and the pH of pure water.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Temperature / K</th>
<th>(K_w) / mol(^2) dm(^{-6})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>273</td>
<td>(1.5 \times 10^{-15})</td>
<td>7.41</td>
</tr>
<tr>
<td>10</td>
<td>283</td>
<td>(3.0 \times 10^{-15})</td>
<td>7.26</td>
</tr>
<tr>
<td>20</td>
<td>293</td>
<td>(6.8 \times 10^{-15})</td>
<td>7.09</td>
</tr>
<tr>
<td>25</td>
<td>298</td>
<td>(1.0 \times 10^{-14})</td>
<td>7.00</td>
</tr>
<tr>
<td>30</td>
<td>303</td>
<td>(1.5 \times 10^{-14})</td>
<td>6.91</td>
</tr>
<tr>
<td>40</td>
<td>313</td>
<td>(3.0 \times 10^{-14})</td>
<td>6.76</td>
</tr>
<tr>
<td>50</td>
<td>323</td>
<td>(5.5 \times 10^{-14})</td>
<td>6.63</td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>(9.5 \times 10^{-14})</td>
<td>6.51</td>
</tr>
</tbody>
</table>
\end{table}
**Weak Bases and Base Ionization Constants**

\[
\text{NH}_3 \text{ (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{NH}_4^+ \text{ (aq)} + \text{OH}^- \text{ (aq)}
\]

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}
\]

- \(K_b\) is the base ionization constant.

**Basicity Constant \(K_b\).**

\[
\text{B(aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{BH}^+ \text{ (aq)} + \text{OH}^- \text{ (aq)}
\]

- The proton accepting strength of a base is quantified in terms of the basicity constant \(K_b\).
- The larger the value of \(K_b\), the stronger the base.
- If \(K_b\) is large then \(pK_b\) will be small, and the stronger will be the base.
- Solve weak base problems like weak acids except solve for [OH\(^-\)] instead of [H\(^+\)].

\[
K_c = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}\]

\[
K_y = K_c[H_2O] = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}
\]

\[
pK_b = -\log_{10} K_b
\]

\[
K_w K_b = K_w
\]

\[
pK_a + pK_b = pK_w
\]
Ionization Constants of Conjugate Acid-Base Pairs

\[
\begin{align*}
HA \text{(aq)} & \rightleftharpoons H^+ \text{(aq)} + A^- \text{(aq)} & K_a \\
A^- \text{(aq)} + H_2O \text{(l)} & \rightleftharpoons OH^- \text{(aq)} + HA \text{(aq)} & K_b \\
H_2O \text{(l)} & \rightleftharpoons H^+ \text{(aq)} + OH^- \text{(aq)} & K_w
\end{align*}
\]

\[K_a K_b = K_w\]

Weak Acid and Its Conjugate Base

\[
K_a = \frac{K_w}{K_b} \quad \text{and} \quad K_b = \frac{K_w}{K_a}
\]

15.7

Acid and base dissociation constants

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ionization Equilibrium</th>
<th>Ionization Constant (K)</th>
<th>(pK_a)</th>
<th>(pK_b)</th>
<th>(pK_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodic acid</td>
<td>HBrO₂ + H₂O \rightleftharpoons HBrO₃⁺ + Br⁻</td>
<td>(1.6 \times 10^{-1})</td>
<td>0.90</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Chlorous acid</td>
<td>HClO₂ + H₂O \rightleftharpoons HClO₃⁺ + ClO₂⁻</td>
<td>(1.1 \times 10^{-2})</td>
<td>1.96</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Chloronic acid</td>
<td>HCl₂O₃ + H₂O \rightleftharpoons HCl₃O₄⁺ + ClO₄⁻</td>
<td>(1.4 \times 10^{-3})</td>
<td>2.85</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃ + H₂O \rightleftharpoons HNO₄⁺ + H₂O⁻</td>
<td>(7.2 \times 10^{-4})</td>
<td>3.14</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HF + H₂O \rightleftharpoons H⁺ + F⁻</td>
<td>(6.6 \times 10^{-4})</td>
<td>3.18</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCO₂H + H₂O \rightleftharpoons HCO₂⁺ + OH⁻</td>
<td>(1.8 \times 10^{-4})</td>
<td>3.74</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>H₃C₆H₄CO₂H + H₂O \rightleftharpoons H₃C₆H₄CO₂⁺ + H₂O⁻</td>
<td>(6.3 \times 10^{-5})</td>
<td>4.20</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>HC₂H₃O₂ + H₂O \rightleftharpoons HC₂H₃O₂⁺ + H₂O⁻</td>
<td>(1.9 \times 10^{-5})</td>
<td>4.72</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>H₂C₂H₃O₂ + H₂O \rightleftharpoons H₂C₂H₃O₂⁺ + H₂O⁻</td>
<td>(1.8 \times 10^{-3})</td>
<td>4.74</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HOCl + H₂O \rightleftharpoons H⁺ + ClO⁻</td>
<td>(2.9 \times 10^{-3})</td>
<td>7.54</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN + H₂O \rightleftharpoons H⁺ + CN⁻</td>
<td>(6.2 \times 10^{-10})</td>
<td>9.25</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>HOCH₃ + H₂O \rightleftharpoons H⁺ + C₆H₅O₂⁻</td>
<td>(1.0 \times 10^{-10})</td>
<td>10.00</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>HO₂ + H₂O \rightleftharpoons H⁺ + H₂O₂⁻</td>
<td>(1.6 \times 10^{-12})</td>
<td>11.74</td>
<td>0.94</td>
<td></td>
</tr>
</tbody>
</table>

**Acid strength**

**Base strength**
Determining a Value of $K_a$ from the pH of a Solution of a Weak Acid.

Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine $K_a$ for butyric acid.

$\text{HC}_4\text{H}_7\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_4\text{H}_7\text{O}_2^- + \text{H}_3\text{O}^+$  \hspace{1cm} $K_a = ?$

For $\text{HC}_4\text{H}_7\text{O}_2$ $K_a$ is likely to be much larger than $K_w$. Therefore assume self-ionization of water is unimportant.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Initial conc.} & 0.250 \text{ M} & 0 & 0 \\
\text{Changes} & -x \text{ M} & +x \text{ M} & +x \text{ M} \\
\text{Equilbrm. conc.} & (0.250-x) \text{ M} & x \text{ M} & x \text{ M} \\
\hline
\end{array}
\]

\[
\log[\text{H}_3\text{O}^+] = -\text{pH} = -2.72
\]

\[
[\text{H}_3\text{O}^+] = 10^{-2.72} = 1.9 \times 10^{-3} = x
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+] [\text{C}_4\text{H}_7\text{O}_2^-]}{[\text{HC}_4\text{H}_7\text{O}_2]} = \frac{1.9 \times 10^{-3} \cdot 1.9 \times 10^{-3}}{(0.250 - 1.9 \times 10^{-3})} = 1.5 \times 10^{-5}
\]

Check assumption: $K_a >> K_w$. 

\[
K_a = 1.5 \times 10^{-5}
\]
**SAMPLE PROBLEM 18.7:** Determining Concentrations from $K_a$ and Initial [HA]

**PROBLEM:** Propanoic acid (CH$_3$CH$_2$COOH, which we simplify and HPr) is an organic acid whose salts are used to retard mold growth in foods. What is the [H$_3$O$^+$] of 0.10M HPr ($K_a = 1.3 \times 10^{-5}$)?

**PLAN:** Write out the dissociation equation and expression; make whatever assumptions about concentration which are necessary; substitute.

Assumptions: For HPr(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + Pr$^-$ (aq)

\[ x = [\text{HPr}]_{diss} = [\text{H}_3\text{O}^+], \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]} \]

**SOLUTION:**

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>HPr(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + Pr$^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10 - 0 0 0</td>
</tr>
<tr>
<td>Change</td>
<td>-x - +x +x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10-x x x</td>
</tr>
</tbody>
</table>

Since $K_a$ is small, we will assume that $x << 0.10$

\[ 1.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]} = \frac{(x)(x)}{0.10} \]

\[ x = \sqrt{(0.10)(1.3 \times 10^{-5})} = 1.1 \times 10^{-3} \text{M} = [\text{H}_3\text{O}^+] \]

Check: [HPr]$_{diss}$ = 1.1 x 10$^{-3}$ M/0.10 M x 100 = 1.1%

**continued**
The relationship between \([\text{H}_3\text{O}^+]\) and \([\text{OH}^-]\) and the relative acidity of solutions.

\[
\begin{align*}
[\text{H}_3\text{O}^+] & > [\text{OH}^-] & & \text{ACIDIC SOLUTION} \\
[\text{H}_3\text{O}^+] & = [\text{OH}^-] & & \text{NEUTRAL SOLUTION} \\
[\text{H}_3\text{O}^+] & < [\text{OH}^-] & & \text{BASIC SOLUTION}
\end{align*}
\]

The pH concept.

- The best quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons \([\text{H}_3\text{O}^+]\) present in a solution.
- The \([\text{H}_3\text{O}^+]\) varies in magnitude over quite a large range in aqueous solution, typically from 1 M to \(10^{-14}\) M.
- Hence to make the numbers meaningful \([\text{H}_3\text{O}^+]\) is expressed in terms of a logarithmic scale called the pH scale.
- The higher the \([\text{H}_3\text{O}^+]\), the more acidic the solution and the lower is the solution pH.

\[
\begin{align*}
pH &= -\log_{10}[\text{H}_3\text{O}^+] \\
[H_3O^+] &= 10^{-pH}
\end{align*}
\]
Strong acids and bases

<table>
<thead>
<tr>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>LiOH</td>
</tr>
<tr>
<td>HBr</td>
<td>NaOH</td>
</tr>
<tr>
<td>HI</td>
<td>KOH</td>
</tr>
<tr>
<td>HClO₄⁻</td>
<td>H₂O</td>
</tr>
<tr>
<td>HNO₃</td>
<td>C₂O₇²⁻</td>
</tr>
<tr>
<td>H₂SO₄⁺</td>
<td>C₂O₇²⁻</td>
</tr>
</tbody>
</table>

*H₂SO₄ ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 687).*

The pH Scale.

- pH is expressed on a numerical scale from 0 to 14.
- When \([H₃O⁺] = 1.0 \text{ M} \) (i.e. \(10^0\text{M}\)), \(p\text{H} = 0\).
- When \([H₃O⁺] = 10^{-14} \text{ M}\), \(p\text{H} = 14\).
- \(p\text{H value < 7}\) implies an acidic solution.
- \(p\text{H value > 7}\) implies an alkaline solution.
- \(p\text{H value = 7}\) implies that the solution is neutral.
- The definition of pH involves logarithms. Hence a change in one pH unit represents a change in concentration of \(H₃O⁺\) ions by a factor of 10.
The pH Values of Some Familiar Aqueous Solutions

Fig. 18.5

The Relations Among $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH

$$pH = -\log_{10}[\text{H}_3\text{O}^+]$$
$$pOH = -\log_{10}[\text{OH}^-]$$
**pH – A Measure of Acidity**

\[
pH = -\log [H^+]\]

<table>
<thead>
<tr>
<th>Solution Is</th>
<th>At 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral</td>
<td>([H^+] = [OH^-])</td>
</tr>
<tr>
<td>acidic</td>
<td>([H^+] &gt; [OH^-])</td>
</tr>
<tr>
<td>basic</td>
<td>([H^+] &lt; [OH^-])</td>
</tr>
</tbody>
</table>

\[
pH \uparrow \quad [H^+] \downarrow
\]

---

**Calculating \([H_3O^+]\), pH, \([OH^-]\), and pOH**

**PROBLEM:** In a restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO₃ to 2.0M, 0.30M, and 0.0063M HNO₃. Calculate \([H_3O^+]\), pH, \([OH^-]\), and pOH of the three solutions at 25°C.

**PLAN:** HNO₃ is a strong acid so \([H_3O^+] = [HNO_3]\). Use \(K_w\) to find the \([OH^-]\) and then convert to pH and pOH.

**SOLUTION:**

For 2.0M HNO₃, \([H_3O^+] = 2.0M\) and \(-\log [H_3O^+] = -0.30 = pH\)

\([OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14}/2.0 = 5.0 \times 10^{-15}M; \ pOH = 14.30\)

For 0.3M HNO₃, \([H_3O^+] = 0.30M\) and \(-\log [H_3O^+] = 0.52 = pH\)

\([OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14}/0.30 = 3.3 \times 10^{-14}M; \ pOH = 13.48\)

For 0.0063M HNO₃, \([H_3O^+] = 0.0063M\) and \(-\log [H_3O^+] = 2.20 = pH\)

\([OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14}/6.3 \times 10^{-3} = 1.6 \times 10^{-12}M; \ pOH = 11.80\)
The problem of acid rain.

Methods for Measuring the pH of an Aqueous Solution

(a) pH paper  (b) Electrodes of a pH meter
**pH Measurement.**

- Approximate pH of a solution determined by use of acid/base indicators:
  - Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.
  - We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.
  - This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3-10.
  - As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.

\[ HIn(aq) + H_2O \rightarrow H_3O^+(aq) + In^- \]

- More accurate pH values determined using an electronic instrument called a pH meter:
  - The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known \([H_3O^+]\) from the external test solution of unknown \([H_3O^+]\)) located at the electrode tip.
  - This membrane potential is proportional to the pH of the test solution.
  - A digital readout of solution pH is obtained.
  - The pH meter is essentially a voltmeter connected to a chemical sensor probe which is sensitive to the concentration of hydrated protons.
  - The pH meter is an example of a potentiometric chemical sensor system. In a potentiometric chemical sensor, the measured voltage is proportional to the logarithm of the analyte concentration.

**pH calculation : strong and weak acids.**

- If acid is strong have complete dissociation then \([H^+]\) can be directly evaluated from stoichiometry of ionization reaction. Hence pH can be evaluated via its defining equation.

- For weak acids have incomplete ionization. To evaluate \([H^+]\) and hence pH we need to evaluate degree of ionization \(\alpha\) and we also require a knowledge of \(K_a\).

\[
\alpha = \sqrt{\frac{K_a}{c}} \\
[H_3O^+] = \sqrt{cK_a} \\
c = [HA] \\
pH = \log_{10}[H_3O^+] = \log_{10}\left(\sqrt{cK_a}\right)
\]
Evaluation of degree of dissociation and pH of weak acid solutions.

\[ \text{HA(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \]

\[ 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

Assume that weak acid dissociation process is predominant and neglect self ionisation of water.

\[ [\text{HA}] = c = \text{initial concentration of weak acid (mol L}^{-1}) \]

\[ \alpha = \text{degree of ionisation} \]

<table>
<thead>
<tr>
<th>Initial concentrations</th>
<th>HA(aq) + H₂O (l)</th>
<th>H₃O⁺ (aq) + A⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(1-(\alpha)) c</td>
<td>(\alpha) c</td>
<td>(\alpha) c</td>
</tr>
</tbody>
</table>

\( 0 < \alpha < 1 \)

The acid dissociation constant is given by:

\[ K_a = \frac{[\text{H}_3\text{O}^+]_{eq} [\text{A}^-]_{eq}}{[\text{HA}]_{eq}} = \frac{\alpha c \cdot \alpha c}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha} \]

We solve for \(\alpha\) to get a quadratic equation:

\[ c\alpha^2 + K_a\alpha - K_a = 0 \]

\[ \alpha = \frac{-K_a + \sqrt{K_a^2 + 4cK_a}}{2c} \]

Once \(\alpha\) is known we can work out \([\text{H}_3\text{O}^+]\) and hence the solution pH since:

Useful approximation.

If \(\alpha\) is small (valid if the acid is weak) then \(\alpha \ll 1\)

We set \(1 - \alpha = 1\)

\[ \alpha \cong \sqrt{\frac{K_a}{c}} \]

\[ [\text{H}_3\text{O}^+] \cong \sqrt{cK_a} \]