Dr Kepert, Chem 1901

Weak Acids and Bases

HA ⇌ H⁺ + A⁻

• Acid dissociation constant
  \[ K_a = \frac{[H^+][A^-]}{[HA]} \]

  pKₐ = – log₁₀ \( K_a \)

More positive pKₐ ⇒ weaker acid (and the stronger the conjugate base)

B + H₂O ⇌ HB⁺ + OH⁻

• Base ionisation constant
  \[ K_b = \frac{[BH^+][OH^-]}{[B]} \]

  pKₐ = – log₁₀ \( K_b \)

More positive pKₐ ⇒ weaker base (and the stronger the conjugate acid)

### Relative Strengths Of Acids And Bases

- Strongest acids lose their protons easily
  - more polarised the H–X bond the greater the acid strength
  - the larger the X, the weaker the bond, the stronger the acid
- Strongest bases hold on to protons strongly
- An acid-base equilibrium always lies in the direction of the weaker acid and weaker base

\[
\text{HCN} + \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COOH} + \text{CN}^-
\]

weaker acid & weaker base ← stronger acid & stronger base

\[ pK_a = 9.2 \quad pK_b = 9.3 \quad pK_a = 4.7 \quad pK_b = 4.8 \]

### Indicators

- Indicator: weak acid ⇐ base
  - each form has a different colour
  - delocalised electrons change energies with protonation
- The pH at which acid ⇨ base depends on the pKₐ of the indicator

  • e.g. phenol red
  
  ![Phenol Red Indicator](image)

### Polyprotic Acids

- Removing more protons is harder:
  - increasing pKₐ: decreasing Kₐ: \( K_{a1} > K_{a2} > K_{a3} \)
  - reason: harder to remove +ve charge against increasing –ve charge
  - large difference in pKₐ values → only need to consider one equilibrium at a time
  (simplifies maths)

### Examples

#### Example from Acids & Bases II

- The pKₐ of formic acid (HCO₂H) is 4.1:
  - find the pH of 1.0 x 10⁻² M NaHCO₂
  - check: it will be basic so expect pH > 7

\[
\begin{align*}
\text{Before:} & \quad 10^{-2} & \quad 0 & \quad 0 \\
\text{After:} & \quad 10^{-2} & \quad x & \quad x \\
& \quad \text{where} & \quad x = \sqrt{10^{-2} \times 10^{-9.3}} = 10^{-5.65}
\end{align*}
\]

\[ \text{pH} = 8.04998 = 8.0 \text{ to two significant figures} \]

What would the pH be for

- 1.05 x 10⁻² M NaHCO₂
  - pH = 8.061
- 0.95 x 10⁻² M NaHCO₂
  - pH = 8.039

### Table 18.5 Successive Kₐ Values for Some Polyprotic Acids at 25°C

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure</th>
<th>Kₐ₁</th>
<th>Kₐ₂</th>
<th>Kₐ₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid (H₂C₂O₄)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>5.5x10⁻²</td>
<td>5.4x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid (H₃PO₄)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>3x10⁻²</td>
<td>1.7x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid (H₂SO₄)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>1.4x10⁻²</td>
<td>6.5x10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid (H₃PO₄)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>7.2x10⁻³</td>
<td>6.3x10⁻⁸</td>
<td>4.2x10⁻¹⁰</td>
</tr>
<tr>
<td>Arsenic acid (H₃AsO₄)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>8x10⁻⁹</td>
<td>1.1x10⁻⁷</td>
<td>3x10⁻¹²</td>
</tr>
<tr>
<td>Citric acid (H₃C₃H₅O₇)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>7.5x10⁻⁴</td>
<td>1.7x10⁻⁵</td>
<td>4.9x10⁻⁷</td>
</tr>
<tr>
<td>Carbonic acid (H₂CO₃)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>4.5x10⁻⁵</td>
<td>4.7x10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>Hydrosulfuric acid (H₂S)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>9x10⁻⁵</td>
<td>1x10⁻¹⁷</td>
<td></td>
</tr>
</tbody>
</table>

*Red trace indicates the ionizable protons.*
Indicators

Examples:

Salts of Weak Acids and Bases

- Is a solution of NaCN acidic or basic?
- Does a solution of NH₄Cl have pH > 7 or < 7?

Another Example

- Rank the following 1.0 M solutions in order of decreasing pH.

<table>
<thead>
<tr>
<th>HNO₃</th>
<th>NaCN</th>
<th>KOH</th>
<th>HCl</th>
<th>CH₂COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₂COOH &gt; NaCN &gt; HNO₃ &gt; HCl &gt; KOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>HNO₃ &gt; HCl &gt; NaCN &gt; KOH &gt; CH₂COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>NaCN &gt; CH₂COOH &gt; KOH &gt; HCl &gt; HNO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>KOH &gt; CH₂COOH &gt; HCl &gt; NaCN &gt; HNO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>KOH &gt; NaCN &gt; CH₂COOH &gt; HNO₃ &gt; HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Salt of a Weak Acid & Weak Base

- What is the pH of ammonium acetate at 25 °C?

Example:
pKₐ of Weak Acid and its Salt

- What is the pH of a solution made up as 0.1 M in acetic acid (HA) and 0.1 M in sodium acetate?

pKₐ of HA = 4.7

- (i.e., take 0.1 mol of HA and 0.1 mol NaA and dilute to 1 L)

Henderson - Hasselbalch Equation

- If ignoring x in added acid & base is valid, i.e. the extent of dissociation is small, then for a solution of weak acid and its conjugate base (salt):

\[
K_a = [H^+] \frac{[\text{added base}]}{[\text{added acid}]}
\]

Convenient but should be checked; if not valid, we can always solve quadratic.

Rearranging, and taking logs, we get the more conventional form of the equation:

\[
pH = pK_a + \log\left(\frac{[\text{added base}]}{[\text{added acid}]}ight)
\]

Buffers

- A solution containing both:
  - a weak acid + its salt.
  - OR
  - a weak base + its salt.

  withstands pH changes when (limited) amounts of acid or base are added.

- Reason: Le Châtelier’s principle.
  - if add acid, then reaction HA ⇌ H⁺ + A⁻ goes to left to absorb change;
  - vice-versa if add base

Example

Consider a buffer solution with 0.1 M each of sodium acetate (NaA) & acetic acid (HA):

(found earlier that pH = 4.7)

What is the pH when 10⁻³ M HCl is added?

Example cont’d

Buffer after addition of H⁺

Buffer with equal concentrations of conjugate base and acid

Buffer after addition of OH⁻