Acids and Bases III

Silberberg 2nd Ed, Chapter 18 & 19
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Weak Acids and Bases

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

- Acid dissociation constant
  \[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]
  \[ pK_a = -\log_{10}K_a \]

More positive p\(K_a\) ⇒ weaker acid (and the stronger the conjugate base)

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

- Base ionisation constant
  \[ K_b = \frac{[\text{H}\text{B}^+][\text{OH}^-]}{[\text{B}]} \]
  \[ pK_b = -\log_{10}K_b \]

More positive p\(K_b\) ⇒ weaker base (and the stronger the conjugate acid)
Relationship between $pK_a$ and $pK_b$

For conjugate systems (Brønsted-Lowry acid-base pairs)

As **acid** (HA):

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

As **conjugate base** (A$^-$):

$$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \quad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_a \times K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$= [\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$pK_a + pK_b = 14$$

Hence only need values of $pK_a$, since $pK_b = 14 - pK_a$
Example from Acids & Bases II

- The $pK_a$ of formic acid ($\text{HCO}_2\text{H}$) is 4.1; find the pH of $1.0 \times 10^{-2}$ M $\text{NaHCO}_2$.

  - (check: it will be basic so expect pH > 7)

$$\text{HCO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HCO}_2\text{H}$$

before: $10^{-2}$ 0 0
after:  $10^{-2} - x$ $x$  $x$

$pK_b = 14 - pK_a = 14 - 4.1 = 9.9$

Thus

$$K_b = \frac{[\text{OH}][\text{HCO}_2\text{H}]}{[\text{HCO}_2^-]}$$

$10^{-9.9} = \frac{x \times x}{10^{-2} - x} \approx \frac{x^2}{10^{-2}}$

$$x = \sqrt{10^{-2} \times 10^{-9.9}} = \sqrt{10^{-11.9}} = 10^{-5.95}$$
Example from Acids & Bases II

• (indeed $x << 10^{-2}$)

  5% rule

• $x = [\text{OH}^-]$ so $pOH = 5.95$;
  $pH = 14 - 5.95 = 8.05$
  $= 8.0$ to two significant figures

When we say $1.0 \times 10^{-2}$ M, experimentally we mean

  $0.95 \times 10^{-2}$ M $< \text{conc} < 1.05 \times 10^{-2}$ M

What would the pH be for

  $1.05 \times 10^{-2}$ M NaHCO$_2$? $pK_a = 4.05$?
  $0.95 \times 10^{-2}$ M NaHCO$_2$? $pK_a = 4.15$?
Example from Acids & Bases II

- The $pK_a$ of formic acid (HCO$_2$H) is 4.1; find the pH of 1.0 x $10^{-2}$ M NaHCO$_2$ 
  
  - (check: it will be basic so expect pH > 7)

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

  before: \(10^{-2}\) \quad 0 \quad 0

  after: \(10^{-2} - x\) \quad x \quad x

  \[
  x = \sqrt{10^{-2} \times 10^{-9.9}} = \sqrt{10^{-11.9}} = 10^{-5.95}
  \]

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

What would the pH be for

- 1.05 x $10^{-2}$ M ? \( \text{pH} = 8.061 \) \( pK_a = 4.05 \) ? \( \text{pH} = 8.075 \)
- 0.95 x $10^{-2}$ M ? \( \text{pH} = 8.039 \) \( pK_a = 4.15 \) ? \( \text{pH} = 8.025 \)
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

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

weaker acid & weaker base $\leftarrow$ stronger acid & stronger base

$\text{p}K_a = 9.2$  $\text{p}K_b = 9.3$  $\text{p}K_a = 4.7$  $\text{p}K_b = 4.8$
Acid Strength

Strong
- HCl → H⁺ + Cl⁻
- H₂SO₄ → H⁺ + SO₄²⁻
- HNO₃ → H⁺ + NO₃⁻
- H₃O⁺ → H⁺ + H₂O
- HSO₄⁻ ⇌ H⁺ + SO₄²⁻
- H₂SO₃ ⇌ H⁺ + HS⁻
- H₃PO₄ ⇌ H⁺ + H₂PO₄⁻
- HF ⇌ H⁺ + F⁻

Medium
- CH₃COOH ⇌ H⁺ + CH₃COO⁻
- H₂CO₃ ⇌ H⁺ + HCO₃⁻
- H₂S ⇌ H⁺ + HS⁻
- HSO₃⁻ ⇌ H⁺ + SO₃²⁻
- H₂PO₄⁻ ⇌ H⁺ + HPO₄²⁻
- NH₄⁺ ⇌ H⁺ + NH₃

Weak
- HCO₃⁻ ⇌ H⁺ + CO₃²⁻
- HPO₄²⁻ ⇌ H⁺ + PO₄³⁻
- H₂O ⇌ H⁺ + OH⁻

Very Weak
- HS⁻ ⇌ H⁺ + S²⁻

Negligible
- OH⁻ ⇌ H⁺ + O²⁻
Polyprotic Acids

\[
\begin{align*}
H_3PO_4 & \rightleftharpoons H^+ + H_2PO_4^- & pK_{a1} &= 2.2 \\
H_2PO_4^- & \rightleftharpoons H^+ + HPO_4^{2-} & pK_{a2} &= 7.2 \\
HPO_4^{2-} & \rightleftharpoons H^+ + PO_4^{3-} & pK_{a3} &= 12.4
\end{align*}
\]

• removing more protons is harder: increasing \( pK_a = \) decreasing \( K_a \): \( K_{a1} > K_{a2} > K_{a3} \)

• reason: harder to remove +ve charge against increasing –ve charge

• large difference in \( pK_a \) values \( \Rightarrow \) only need to consider one equilibrium at a time

  (simplifies maths)
<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure*</th>
<th>( K_{a1} )</th>
<th>( K_{a2} )</th>
<th>( K_{a3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid (H(_2)C(_2)O(_4))</td>
<td><img src="image1" alt="Lewis Structure" /></td>
<td>( 5.6 \times 10^{-2} )</td>
<td>( 5.4 \times 10^{-5} )</td>
<td></td>
</tr>
<tr>
<td>Phosphorous acid (H(_3)PO(_3))</td>
<td><img src="image2" alt="Lewis Structure" /></td>
<td>( 3 \times 10^{-2} )</td>
<td>( 1.7 \times 10^{-7} )</td>
<td></td>
</tr>
<tr>
<td>Sulfurous acid (H(_2)SO(_3))</td>
<td><img src="image3" alt="Lewis Structure" /></td>
<td>( 1.4 \times 10^{-2} )</td>
<td>( 6.5 \times 10^{-8} )</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid (H(_3)PO(_4))</td>
<td><img src="image4" alt="Lewis Structure" /></td>
<td>( 7.2 \times 10^{-3} )</td>
<td>( 6.3 \times 10^{-8} )</td>
<td>( 4.2 \times 10^{-13} )</td>
</tr>
<tr>
<td>Arsenic acid (H(_3)AsO(_4))</td>
<td><img src="image5" alt="Lewis Structure" /></td>
<td>( 6 \times 10^{-3} )</td>
<td>( 1.1 \times 10^{-7} )</td>
<td>( 3 \times 10^{-12} )</td>
</tr>
<tr>
<td>Citric acid (H(_3)C(_6)H(_5)O(_7))</td>
<td><img src="image6" alt="Lewis Structure" /></td>
<td>( 7.5 \times 10^{-4} )</td>
<td>( 1.7 \times 10^{-5} )</td>
<td>( 4.0 \times 10^{-7} )</td>
</tr>
<tr>
<td>Carbonic acid (H(_2)CO(_3))</td>
<td><img src="image7" alt="Lewis Structure" /></td>
<td>( 4.5 \times 10^{-7} )</td>
<td>( 4.7 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Hydrosulfuric acid (H(_2)S)</td>
<td><img src="image8" alt="Lewis Structure" /></td>
<td>( 9 \times 10^{-8} )</td>
<td>( 1 \times 10^{-17} )</td>
<td></td>
</tr>
</tbody>
</table>

*Red type indicates the ionizable protons.
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 $pK_a$ of the indicator

- e.g. phenol red

![Chemical structures of phenol red in its yellow and red forms]
Indicators

- Crystal violet
- Thymol blue
- 2,4-Dinitrophenol
- Bromphenol blue
- Bromcresol green
- Methyl red
- Alizarin
- Bromthymol blue
- Phenol red
- Phenolphthalein
- Alizarin yellow R

Silberberg Fig 19.4  p 815
Examples:
Salts of Weak Acids and Bases

- Is a solution of NaCN acidic or basic?
  - NaCN is the salt of NaOH (strong base) and HCN (weak acid). The base “wins” pH > 7
  - overall reaction is
    \[ \text{H}_2\text{O} + \text{CN}^- \rightarrow \text{OH}^- + \text{HCN} \]

- Does a solution of NH\(_4\)Cl have pH > 7 or < 7?
  - Salt of NH\(_4\)OH (weak base) and HCl (strong acid)
  - acid “wins” pH < 7 and reaction is
    \[ \text{H}_2\text{O} + \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+ \]
Another Example

• Rank the following 1.0 M solutions in order of decreasing pH.
  HNO$_3$  NaCN  KOH  HCl  CH$_3$COOH

<table>
<thead>
<tr>
<th>Letter</th>
<th>Solution Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH$_3$COOH &gt; NaCN &gt; HNO$_3$ &gt; HCl &gt; KOH</td>
</tr>
<tr>
<td>B</td>
<td>HNO$_3$ &gt; HCl &gt; NaCN &gt; KOH &gt; CH$_3$COOH</td>
</tr>
<tr>
<td>C</td>
<td>NaCN &gt; CH$_3$COOH &gt; KOH &gt; HCl &gt; HNO$_3$</td>
</tr>
<tr>
<td>D</td>
<td>KOH &gt; CH$_3$COOH &gt; HCl &gt; NaCN &gt; HNO$_3$</td>
</tr>
<tr>
<td>E</td>
<td>KOH &gt; NaCN &gt; CH$_3$COOH &gt; HNO$_3$ &gt; HCl</td>
</tr>
</tbody>
</table>
Salt of a Weak Acid & Weak Base

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

2 possible reactions are:

\[
\begin{align*}
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- & K_b = 10^{-9.24} \\
\text{NH}_4^+ + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ & K_a = 10^{-9.24}
\end{align*}
\]

- Anions of weak acids hydrolyse → OH\(^-\)
- Cations of weak bases hydrolyse → H\(_3\)O\(^+\)

\textbf{In this case }K_a = K_b \text{ so salt is neutral!}

Salts of Strong acids & Strong bases always neutral

DEMONSTRATION
Example:
\(pK_a\) 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?

\(pK_a\) of HA = 4.7
  
  (i.e., take 0.1 mol of HA and 0.1 mol NaA and dilute to 1 L)

Can work either from acid or base dissociation constants. Take acid this time:

\[
\ce{HA \rightleftharpoons H^+ + A^-}
\]

(before:

|   | 0.1 | 0   | 0.1 |

(after:

|   | 0.1 – \(x\) | \(x\) | 0.1 + \(x\) |

\((x\ \text{mol HA dissociates \& forms } x\ \text{mol of A}^-)\)
Example cont’d: pK\textsubscript{a} of Weak Acid and its Salt

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

\[ K_a = 10^{-4.7} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x \ (0.1 + x)}{0.1 - x} \]

could solve as quadratic, but make usual assumption that \( x \ll 0.1 \)

then \( 10^{-4.7} \approx \frac{x \ (0.1)}{0.1}; \ x = 10^{-4.7} \)

(check: \( << 0.1 \) )

\( \text{pH} = - \log x = 4.7 \)

= pK\textsubscript{a}
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):

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

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:

$$pH \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]}$$
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 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ goes to left to absorb change;
  – vice-versa if add base
**Example**

- Find pH of solution which is 0.1 M in NH$_4^+$ and 0.2 M in NH$_3$ where p$K_a$ of NH$_4^+$ = 9.2

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

  before: \quad 0.2 \quad 0.1 \quad 0

  after: \quad 0.2 - x \quad 0.1 + x \quad x

  \[
  pK_b = 14 - 9.2 = 4.8
  \]

  \[
  K_b = 10^{-4.8} = \frac{(0.1 + x)x}{0.2 - x} \approx \frac{0.1x}{0.2}
  \]

  \[
  x = 0.2/0.1 \times 10^{-4.8} \quad (\text{indeed} \; x \ll 0.1)
  \]

  \[
  \text{pOH} = -\log x = 4.5
  \]

  \[\Rightarrow \text{pH} = 9.5\]
Effect of pH Change on Buffer

- Consider change in pH of pure water (pH = 7) if we add $10^{-3}$ M HCl:

  \[
  [H^+] = 10^{-3} \text{ M (can neglect amount already present in water)}, \text{ so pH goes from 7 to 3}
  \]

  Huge change!

  What about buffers?
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?

$$
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-
$$

initially: $0.1$ $10^{-3}$ $0.1$

eqm: $0.1+10^{-3}-x$ $x$ $0.1-10^{-3} + x$

i.e., suppose all but $x$ of the added H$^+$ → HA

but $x$ will be very small...

$$K_a = 10^{-4.7} = \frac{x (0.1-10^{-3} + x)}{0.1 + 10^{-3} - x} \approx \frac{x (0.1-10^{-3})}{0.1 + 10^{-3}}$$
\[ x = 1.02 \times K_a = 0.000020 << 0.001 \]

\[ \text{pH} = \log x = 4.69 \]

- the pH hardly changes from 4.7!

Solution is *buffered* against pH change.