Definitions of pH and pOH

Because of large concentration range (between about 10 M and 10^{-15} M) a logarithmic scale of concentrations is defined:

\[ \text{pH} = -\log[H^+] \]
\[ \text{pOH} = -\log[OH^-] \]

Relationship of pH and pOH

Since \([H^+][OH^-] = 10^{-14}\)

\[-\log[H^+] + -\log[OH^-] = -\log[10^{14}]\]

\[ \text{pH} + \text{pOH} = 14 \]

So \(\text{pH} = 14 - \text{pOH}\) and \(\text{pOH} = 14 - \text{pH}\)

Neutral solution, \(\text{pH} = \text{pOH} = 7\)

Acid solutions, \([H^+] > [OH^-]\), \(\text{pH} < 7\)

Basic solutions, \([H^+] < [OH^-]\), \(\text{pH} > 7\)

(See Table 2.2)

Review of Logarithmic Calculations

- What is pH if \([H^+]\) is \(3.2 \times 10^{-4} \text{ M}\)?
  \[
  \log 3.2 \times 10^{-4} = \log 3.2 + \log 10^{-4} \\
  = 0.51 (\text{the mantissa}) - 4 (\text{the characteristic}) \\
  = -3.49 \\
  \text{so } \text{pH} = -(-3.49) = 3.49
  \]

- What is \([H^+]\) if pH is 8.56?
  \[
  [H^+] = 10^{8.56} = 10^4 \times 10^{-0.5} = 10^4 \times 10^{-9} \\
  = 2.75 \times 10^{-5}
  \]
Need Review in such calculations?

- Visit the pH drill web site
- Visit your textbook web site

Strong Acids versus Weak Acids

- Strong acids completely dissociate
  - $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
  - $[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$  
  - concentration will be given by HCl concentration unless it is low enough that OH$^-$ cannot be ignored.
- Weak acids partly dissociate. The extent of dissociation can be expressed by an equilibrium constant, $K_a$

Other strong acids are HNO$_3$, HBr, HI, H$_2$SO$_4$(first proton dissociation), HClO$_3$, and HClO$_4$. Note that a $10^{-9}$ M solution of HCl would not have a pH of 9! You could not ignore the hydroxide concentration then, and would need to solve the equation $[\text{H}^+] = [\text{Cl}^-] + \frac{\text{Kw}}{[\text{H}^+]}$, where you substitute $\frac{\text{Kw}}{[\text{H}^+]}$ for $[\text{OH}^-]$.

Weak Acid Dissociation

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$
- or

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

- $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
Calculation of $[H^+]$ for a Weak Acid ($[HA]=c$)

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{x^2}{c-x}$$

- If $x < 0.05c$, $K_a = \frac{x^2}{c}$ and $x = \sqrt{K_a c}$
- If $x \geq 0.05c$, $x^2 + K_a x + K_a c = 0$
  - and $x = \frac{-K_a \pm \sqrt{K_a^2 - 4K_a c}}{2}$

Try the formula $(K_a c)^{1/2}$ first to see if $x$ is small enough relative to $c$ to ignore. If not, then you need to use the quadratic equation. Note we are assuming that $[H^+] = [A^-]$, when actually $[H^+] = [A^-] + [OH^-]$. But if the solution is acidic, $[H^+] >> [OH^-]$ and the hydroxide term can be ignored. That might not be the case for very dilute solutions, or for $K_a$’s approaching 7 and above. For $K_a$’s above 7, the calculation should probably be done using $K_h$.

Henderson-Hasselbalch Equation

- Rearrange $K_a$ expression:
  $$[H^+] = \frac{[HA]}{[A^-]}$$
- Take logarithm:
  $$\log[H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$
  $$\text{pH} = pH + \log \frac{[A^-]}{[HA]}$$

Note there is a direct proportional relationship between the hydrogen ion concentration and the ratio of protonated forms. When $[H^+] = K_a$, then $[HA]/[A^-] = 1$.

A Base Can Be Treated As an Acid

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

- can also be written as: $BH^+ \rightleftharpoons B + H^+$
- $K_b = \frac{[BH^+]}{[B][H^+]}$
  - and $K_b = \frac{[B][H^+]}{[BH^+]}, \frac{[BH^+][OH^-]}{[B]} = [H^+][OH^-] = K_w$
**Slide 10**

**Difference in an “Acid” and a “Base” Dissociation**

- HA → H⁺ + A⁻
  - Charge separation; dielectric constant affects $K_a$
- BH⁺ → H⁺ + B
  - No charge separation; no dielectric constant affect on $K_a$

**Slide 11**

**Titration of a Weak Acid with a Strong Base**

- A strong base added to the equilibrium solution of the weak acid will consume the H⁺, converting HA to A⁻.

\[
\text{HA} + \text{OH} \rightarrow \text{A}^- + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Before</th>
<th>10 mmol</th>
<th>x mmol</th>
<th>small</th>
</tr>
</thead>
<tbody>
<tr>
<td>After</td>
<td>(10-x) mmol</td>
<td>small</td>
<td>x mmol</td>
</tr>
</tbody>
</table>

\[pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) = pK_a + \log \left( \frac{x \text{ mmol/volume}}{(10-x) \text{ mmol/volume}} \right)\]

- This equation leads to the graph of Figure 2.12

**Slide 12**

**Distinguish Between Fraction of Base Form and Ratio of Base/Acid**

<table>
<thead>
<tr>
<th>HA</th>
<th>A⁻</th>
<th>A⁻/HA</th>
<th>A⁻/(HA+A⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 mmol</td>
<td>10 mmol</td>
<td>10/90=0.11</td>
<td>10/100=0.10</td>
</tr>
<tr>
<td>75 mmol</td>
<td>25 mmol</td>
<td>25/75=0.33</td>
<td>25/100=0.25</td>
</tr>
<tr>
<td>50 mmol</td>
<td>50 mmol</td>
<td>50/50=1.0</td>
<td>50/100=0.50</td>
</tr>
<tr>
<td>25 mmol</td>
<td>75 mmol</td>
<td>75/25=3.0</td>
<td>75/100=0.75</td>
</tr>
<tr>
<td>10 mmol</td>
<td>90 mmol</td>
<td>90/10=9.0</td>
<td>90/100=0.90</td>
</tr>
</tbody>
</table>

Note that the ratio in the logarithm turn can be a ratio of quantity (moles) as well as a ratio of concentrations, because the volume is the same for both the numerator and denominator.
Sketching Titration Curves

- According to ratio of $A^-/HA$

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Ratio</th>
<th>Log(ratio)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.11</td>
<td>-0.96</td>
<td>$pK_a-0.96$</td>
</tr>
<tr>
<td>0.25</td>
<td>0.33</td>
<td>-0.48</td>
<td>$pK_a-0.48$</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>0.0</td>
<td>$pK_a$</td>
</tr>
<tr>
<td>0.75</td>
<td>3.0</td>
<td>0.48</td>
<td>$pK_a+0.48$</td>
</tr>
<tr>
<td>0.90</td>
<td>9.0</td>
<td>0.95</td>
<td>$pK_a+0.95$</td>
</tr>
</tbody>
</table>

Rough rule of thumb:
- 1% titration, $pH = pK-2$
- 10% titration, $pH = pK-1$
- 50% titration, $pH = pK$
- 90% titration, $pH=pK+1$
- 99% titration, $pH=pK+2$

These calculations assume that $[A^-]=$concentration of hydroxide added. That is not necessarily the case for acids with very low $pK$’s, because you also have to take into account the $A^-$ formed in the dissociation of the acid before you started adding base.

Sketching Titration Curves (con’t)

- The shape of all curves are the same
- The position of the curves varies with $pK_a$
  - See Figure 2.13
- Curves for diprotic and triprotic acids can be laid from end to end
  - See Figure 2.14

Buffers

- A weak acid and its conjugate base constitute a buffer
- Buffers resist change in pH
- Buffers are most effective at the pk of the weak acid
- Buffer capacity depends on concentration
- Refer to Figure 2.15
- See Textbook website discussion of buffers
Phosphate Buffer

- Best buffer at its pK's; pK$_2$ most physiologically relevant
  - pK$_1$=2.15, pK$_2$=7.20, pK$_3$=12.40
- As a take-home exercise, calculate the concentration of all ionic species of phosphate ([H$_3$PO$_4$], [H$_2$PO$_4^-$], [HPO$_4^{2-}$], and [PO$_4^{3-}$]) in 0.01 M total phosphate at pH 7.4 (the pH of blood).

Hint for Phosphate Calculation

- You have three equilibrium equations
  - For K$_1$, K$_2$, and K$_3$
- You have one conservation equation
  - $[H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}]=0.01$ M
- Four equations and four unknowns can be solved by simultaneous equations. There are several algebraic ways to proceed.

Bicarbonate Buffer

- A major buffer in blood
- Also in equilibrium with gaseous CO$_2$
- Relevant equations:
  $$\text{CO}_2(g) \rightleftharpoons \text{CO}_2(d)$$
  $$\text{CO}_2(d) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$
  $$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$$
Bicarbonate Buffer, (con’t)

- The pK₁ recorded for bicarbonate depends on whether you are referring to \([H_2CO_3]\) alone, or “total dissolved CO₂” which is \([H_2CO_3] + [CO_2(d)]\) \(([CO_2]/[H_2CO_3] = 500)\)

\[
pH = pK_1 + \log \frac{[HCO^-]}{[H_2CO_3]}
\]
then \(pK_1 = 3.57\)

\[
pH = pK_{(overall)} + \log \frac{[HCO^-]}{[H_2CO_3] + [CO_2(d)]}
\]
then \(pK_{(overall)} = 6.1\)

While a normal titration is plotting the curve for \(pH = pK + \log(x/c-x)\), when carbonic acid is titrated the concentration of the acid does not decrease because it is replenished by the gaseous CO₂ in equilibrium with the solution. So the equation becomes \(pH = pK + \log(x/c)\), and this curve does not turn up, but keeps getting flatter. Hence bicarbonate is a better buffer at 7.4 than at 6.1, even though that is more than one pH unit above the pK.

Laboratory Buffers

- Most laboratory experiments require the use of buffers to control the pH. Phosphate buffer is often used, but a number of other buffers referred to as the “Good” buffers (after N.E.Good) have been developed for experimental use.