\[ K_{eq} \text{(55.5 M)} = [H^+] [OH^-] \]

\[ K_w = [H^+] [OH^-] = 1.0 \times 10^{-14} \text{ M}^2 \]

- Kw is called the ion product for water

<table>
<thead>
<tr>
<th>pH</th>
<th>[H(^+)] (M)</th>
<th>[OH(^-)] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>10^{-14}</td>
</tr>
<tr>
<td>1</td>
<td>10^{-1}</td>
<td>10^{-13}</td>
</tr>
<tr>
<td>2</td>
<td>10^{-2}</td>
<td>10^{-12}</td>
</tr>
<tr>
<td>3</td>
<td>10^{-3}</td>
<td>10^{-11}</td>
</tr>
<tr>
<td>4</td>
<td>10^{-4}</td>
<td>10^{-10}</td>
</tr>
<tr>
<td>5</td>
<td>10^{-5}</td>
<td>10^{-9}</td>
</tr>
<tr>
<td>6</td>
<td>10^{-6}</td>
<td>10^{-8}</td>
</tr>
<tr>
<td>7</td>
<td>10^{-7}</td>
<td>10^{-7}</td>
</tr>
<tr>
<td>8</td>
<td>10^{-8}</td>
<td>10^{-6}</td>
</tr>
<tr>
<td>9</td>
<td>10^{-9}</td>
<td>10^{-5}</td>
</tr>
<tr>
<td>10</td>
<td>10^{-10}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>11</td>
<td>10^{-11}</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>12</td>
<td>10^{-12}</td>
<td>10^{-2}</td>
</tr>
<tr>
<td>13</td>
<td>10^{-13}</td>
<td>10^{-1}</td>
</tr>
</tbody>
</table>
What is pH?

\[ \text{pH} = \log_{10}(1/[H^+]) = -\log_{10}[H^+] \]
Example:

Find the $K_a$ of a 0.04 M weak acid HA whose $[H^+]$ is $1 \times 10^{-4}$?

$$K_a = \frac{[A^-][H^+]}{[HA]} = \frac{[H^+]^2}{[HA]} = \frac{10^{-4} \times 10^{-4}}{0.04} = 2.5 \times 10^{-7}$$

Example:

What is the $[H^+]$ of a 0.05 M Ba(OH)$_2$?

$$[OH^-] = 2 \times 0.05 = 0.10 \text{ M} = 1 \times 10^{-1}$$

$$[H^+] = 1 \times 10^{-13}$$
Example:

The [H⁺] of a 0.03 M weak base solution is 1 x 10⁻¹⁰ M. Calculate pKb?

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

\[ [\text{OH}^-] = 10^{-4} \]

\[ K_b = \frac{(10^{-4} \times 10^{-4})}{0.03} = 3.33 \times 10^{-7} \text{ M} \]

\[ pK_b = -\log K_b = 6.48 \]
Exercises

What is the pH of

- 0.01 M HCl?
- 0.01 N H₂SO₄?
- 0.01 N NaOH?
- 1 x 10⁻¹¹ HCl? (this is a tricky one)
- 0.1 M of acetic acid (CH₃COOH)? Remember Ka
Determination of pH

- **Acid-base indicator**
  - Litmus paper (least accurate)
  - Universal indicator
- **An electronic pH meter (most accurate)**
The Henderson-Hasselbalch equation is:

\[ \text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} \]

where \( \text{pK}_a \) is the pH where 50% of the acid is dissociated into its conjugate base.
Maintenance of equilibrium

Le Châtelier’s principle

When more reactants, A and/or B is added, the equilibrium shifts to reduce A and B by producing more C and D.

\[ A + 2B \rightleftharpoons C + D \]

When more products, C and/or D is added, the equilibrium shifts to reduce C and D by producing more A and B.
A comparison of the change in pH (water vs. acetic acid)

0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of a 0.10 M acetic acid 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.
Buffers are solutions that resist changes in pH by changing reaction equilibrium.

They are composed of mixtures of a weak acid and a roughly equal concentration of its conjugate base.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOH</td>
<td>CH₃COONa (NaCH₃COO)</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>NaH₂PO₄</td>
</tr>
<tr>
<td>H₂PO₄⁻ (or NaH₂PO₄)</td>
<td>Na₂HPO₄</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>NaHCO₃</td>
</tr>
</tbody>
</table>
Titration curve of buffer

What is the midpoint?

Equivalence point

What is the ratio of the conjugate base:acid at the different points?

Buffering capacity
A buffer is made by combining weak acid/base and its salt.

The ability of a buffer to function depends on:
- Buffer concentration
- Buffering capacity
- pKa of the buffer
- The desired pH
Exercise

A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8. Hence, the pH of the solution is given by

\[ pH = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1 \]

Similarly, the pKa of an acid can be calculated.
Exercise

Predict then calculate the pH of a buffer containing
- 0.1M HF and 0.12M NaF? (Ka = 3.5 x 10^{-4})
- 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?

What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)

What is the concentration of 5 ml of acetic acid knowing that 44.5 ml of 0.1 N of NaOH are needed to reach the end of the titration of acetic acid? Also, calculate the normality of acetic acid.

The number of equivalents of OH- required for complete neutralization is equal to the number of equivalents of hydrogen ion present as H+ and HA.
Titration curve of phosphate buffer

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons pK_{a(1)} = 2.14 & \text{H}_2\text{PO}_4^- & \rightleftharpoons pK_{a(2)} = 7.20 \\
+ & & + \\
\text{H}^+ & & \text{H}^+ \\
\text{HPO}_4^{2-} & \rightleftharpoons pK_{a(3)} = 12.4 & \text{PO}_4^{3-} & \\
+ & & + \\
\text{H}^+ & & \\
\end{align*}
\]

Third midpoint
\[\left[\text{HPO}_4^{2-}\right] = \left[\text{PO}_4^{3-}\right] \]
\[pK_a = 12.7\]

Second midpoint
\[\left[\text{H}_2\text{PO}_4^-\right] = \left[\text{HPO}_4^{2-}\right] \]
\[pK_a = 7.2\]

First midpoint
\[\left[\text{H}_3\text{PO}_4\right] = \left[\text{H}_2\text{PO}_4^-\right] \]
\[pK_a = 2.2\]

Note values

\[
\begin{align*}
\text{pH} & \quad \text{Equivalents of OH}^- \\
14 & \quad 0.5 \\
12 & \quad 1.0 \\
10 & \quad 1.5 \\
8 & \quad 2.0 \\
6 & \quad 2.5 \\
4 & \quad 3.0 \\
2 & \\
0 & \\
\end{align*}
\]
What is the pKa of a dihydrogen phosphate buffer when pH of 7.2 is obtained when 100 ml of 0.1 M NaH$_2$PO$_4$ is mixed with 100 ml of 0.1 M Na$_2$HPO$_4$?

a) A solution was prepared by dissolving 0.02 moles of acetic acid (HOAc; pKa = 4.8) in water to give 1 liter of solution. What is the pH?

b) To this solution was then added 0.008 moles of concentrated sodium hydroxide (NaOH). What is the new pH? (In this problem, you may ignore changes in volume due to the addition of NaOH).
Buffers in human body

- Carbonic acid-bicarbonate system (blood)
- Dihydrogen phosphate-monohydrogen phosphate system (intracellular)
  - ATP, glucose-6-phosphate, bisphosphyglycerate (RBC)
- Proteins (why?)
  - Hemoglobin in blood
  - Other proteins in blood and cells
**Bicarbonate buffer**

\[
\text{CO}_2(d) + \text{H}_2\text{O} \rightleftharpoons K_b \text{H}_2\text{CO}_3
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons K_a \text{H}^+ + \text{HCO}_3^-
\]

Blood (instantaneously)

**CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-

Lungs (within minutes)

Excretion via kidneys (hours to days)
Titration curve of bicarbonate buffer

Note pKa

% buffer in the form of $\text{HCO}_3^-$

$\text{pH}$

% buffer in the form of $\text{H}_2\text{CO}_3$ and $\text{CO}_2$

Region of maximum buffering capacity

Normal blood pH

$pK = 6.1$
Why is this buffer effective?

Even though the normal blood pH of 7.4 is outside the optimal buffering range of the bicarbonate buffer, which is 6.1, this buffer pair is important due to two properties:

- Bicarbonate is present in a relatively high concentration in the ECF (24mmol/L).
- The components of the buffer system are effectively under physiological control: the CO₂ by the lungs, and the bicarbonate by the kidneys.

It is an open system (not a closed system like in laboratory)

An open system is a system that continuously interacts with its environment.
Acidosis and alkalosis

Both pathological conditions can be either metabolic or respiratory.

Acidosis (pH < 7.35)
- Metabolic: production of ketone bodies (starvation)
- Respiratory: pulmonary (asthma; emphysema)

Alkalosis (pH > 7.45)
- Metabolic: administration of salts
- Respiratory: hyperventilation (anxiety)
Respiratory conditions

**Respiratory Acidosis**

\[ H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow \text{CO}_2 + H_2O \]

**Respiratory Alkalosis**

\[ H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow \text{CO}_2 + H_2O \]
Metabolic conditions

**Metabolic Acidosis**

\[H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O\]

**Metabolic Alkalosis**

\[H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O\]
Causes of respiratory acid-base disorders

Acidosis:
- Choking
- Bronchopneumonia
- COAD

Alkalosis:
- Hysterical overbreathing
- Mechanical over-ventilation
- Raised intracranial pressure
Causes of metabolic acid-base disorders

**Acidosis**
- Impaired $H^+$ excretion
- Increased $H^+$ production or ingestion
- Loss of $HCO_3^-$

**Alkalosis**
- Loss of $H^+$ in vomit
- Alkali ingestion
- Potassium deficiency
Compensation: The change in HCO$_3^-$ or pCO$_3$ that results from the primary event.

If underlying problem is metabolic, hyperventilation or hypoventilation can help: **respiratory compensation**.

If problem is respiratory, renal mechanisms can bring about **metabolic compensation**.

May be **complete** if brought back within normal limits.

**Partial compensation** if range is still outside norms.
<table>
<thead>
<tr>
<th>Acid-Base Disorder Change</th>
<th>Primary Change</th>
<th>Compensatory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Respiratory acidosis</td>
<td>pCO₂ up</td>
<td>HCO₃⁻ up</td>
</tr>
<tr>
<td>Respiratory alkalosis</td>
<td>pCO₂ down</td>
<td>HCO₃⁻ down</td>
</tr>
<tr>
<td>Metabolic acidosis</td>
<td>HCO₃⁻ down</td>
<td>PCO₂ down</td>
</tr>
<tr>
<td>Metabolic alkalosis</td>
<td>HCO₃⁻ up</td>
<td>PCO₂ up</td>
</tr>
</tbody>
</table>

\[ H^+ (aq) + HCO_3^- (aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g) \]
<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>pCO(_2)</th>
<th>HCO(_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resp. acidosis</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>But&lt;7.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resp. alkalosis</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>but&gt;7.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Met. Acidosis</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>but&lt;7.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Met. alkalosis</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>but&gt;7.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Partially compensated

\[
\text{H}^+_{(aq)} + \text{HCO}_3^-_{(aq)} \leftrightarrow \text{H}_2\text{CO}_3_{(aq)} \leftrightarrow \text{H}_2\text{O}_{(l)} + \text{CO}_2_{(g)}
\]

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>pCO(_2)</th>
<th>HCO(_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Res. Acidosis</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Res. Alkalosis</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Met. Acidosis</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Met. Alkalosis</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
</tbody>
</table>