Electrolytes

- Solutes which improve the conductivity of a solution are called electrolytes.
- A solution which conducts electricity is known as an electrolyte solution.
- Pure water is a non-electrolyte. Water containing salt such as NaCl is an electrolyte solution (due to the presence of ions in solution)
- NaCl and other salts don’t just dissolve, they dissociate in water.
- Ions that were packed together in the crystal separate upon dissolving and become individual (solvated) ions in the solution.

- We write this in form of dissociation equations (to keep track of the number of ions per formula unit)
  \[
  \text{NaCl(s)} \leftrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)
  \]
  \[
  \text{K}_2\text{CO}_3(s) \leftrightarrow 2 \text{K}^+(aq) + \text{CO}_3^{2-}(aq)
  \]
  (s) denotes solid; (aq) denotes aqueous (in water)

Ion Concentrations

- A solution of just NaCl and water has equal concentrations of sodium and chloride ions
- For example in a 0.1 M NaCl we have:
  \[
  \text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)
  \]
  \[
  0.1 \text{ mol} \rightarrow 0.1 \text{ mol} + 0.1 \text{ mol}
  \]
  Thus in a 0.1 M NaCl the concentration of chloride ions is 0.1 mol/L and the concentration of sodium ions is also 0.1 mol/L.

- How about a 0.1 M CaCl$_2$ we have:
  \[
  \text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)
  \]
  \[
  0.1 \text{ mol} \rightarrow 0.1 \text{ mol} + 0.2 \text{ mol}
  \]
  Thus in a 0.1 M CaCl$_2$ solution concentration of chloride ions is 0.2 mol/L and the concentration of sodium ions is 0.1 mol/L.

Exercise: What has the greatest amount of chloride ions

- 1.2 L of 0.50 M NaCl, 1.1 L of 0.40 M CaCl$_2$, 0.75 L of 0.40 M AlCl$_3$, 2.0 L of 0.50 M KClO$_3$ or 30 L of 0.001 M Cl$_2$
Ionization

• Sugars dissolve in water but do not dissociate (don’t form ions) Why? The bonds in the sugar molecules are covalent, not ionic!

\[ C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq) \]

• However if the bonds are very polar they might break in water leading to ions after all:

\[ \text{HCl(g)} \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \]

The HCl molecules have been split apart by the water resulting in the formation of ions. Acids are electrolytes.

• Strong acids ionize completely and their solutions contain high concentrations of H\(^+\) ions.

• Strong acids are strong electrolytes. For example HNO\(_3\), H\(_2\)SO\(_4\), HClO\(_4\)

• Weak acids ionize incompletely and their solutions contain lower concentrations of H\(^+\) ions.

• Weak acids are weak electrolytes.

Some definitions of acids

• Arrhenius Theory

   Acids are proton donors whilst bases are hydroxide ion donors.

• Brønsted Theory

   Acids are proton donors whilst bases are proton acceptors.

• Lewis Theory

   Acids are electron pair acceptors whilst bases are electron pair donors

pH

• The pH scale is a convenient way of referring to the degree of acidity of a solution.

• pH is the negative decadic logarithm of the H\(^+\) ion concentration: \(pH = -\log [H^+]\)

• So pure water has a pH of 7 meaning the concentration of H\(^+\) is \(10^{-7}\) mol/l = 0.0000001 M

• This comes from the dissociation of water itself (very slight)

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

We see from this equation that there is an equal concentration of H\(^+\) and OH\(^-\) (neutral).
Ion-Product Constant \( K_w = 1.0 \times 10^{-14} = [H_3O^+] [OH^-] \)  

- Let’s take the –log of expression (1).
- \(-\log K_w = -\log(1.0 \times 10^{-14}) = -\log([H_3O^+][OH^-])\)
- \(pK_w = 14 = -\{\log[H_3O^+] + \log[OH^-]\}\)
- \(pK_w = 14 = \text{pH} + \text{pOH} \text{ in all aqueous solutions}\)

<table>
<thead>
<tr>
<th>Substance</th>
<th>([H^+]) (M)</th>
<th>pH</th>
<th>([OH^-]) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric juice</td>
<td>1 (1 \times 10^{-6})</td>
<td>6.0</td>
<td>1 \times 10^{-14}</td>
</tr>
<tr>
<td>Lemon juice</td>
<td>1 \times 10^{-5}</td>
<td>7.0</td>
<td>1 \times 10^{-13}</td>
</tr>
<tr>
<td>Cola, vinegar</td>
<td>1 \times 10^{-4}</td>
<td>8.0</td>
<td>1 \times 10^{-12}</td>
</tr>
<tr>
<td>Wine</td>
<td>1 \times 10^{-3}</td>
<td>9.0</td>
<td>1 \times 10^{-11}</td>
</tr>
<tr>
<td>Tomatoes</td>
<td>1 \times 10^{-2}</td>
<td>10.0</td>
<td>1 \times 10^{-10}</td>
</tr>
<tr>
<td>Bananas</td>
<td>1 \times 10^{-1}</td>
<td>11.0</td>
<td>1 \times 10^{-9}</td>
</tr>
<tr>
<td>Black coffee</td>
<td>1 \times 10^{-2}</td>
<td>12.0</td>
<td>1 \times 10^{-8}</td>
</tr>
<tr>
<td>Rain</td>
<td>1 \times 10^{-3}</td>
<td>13.0</td>
<td>1 \times 10^{-7}</td>
</tr>
<tr>
<td>Saliva</td>
<td>1 \times 10^{-4}</td>
<td>14.0</td>
<td>1 \times 10^{-6}</td>
</tr>
<tr>
<td>Milk</td>
<td>1 \times 10^{-5}</td>
<td>15.0</td>
<td>1 \times 10^{-5}</td>
</tr>
<tr>
<td>Human blood</td>
<td>1 \times 10^{-5}</td>
<td>16.0</td>
<td>1 \times 10^{-4}</td>
</tr>
<tr>
<td>Seawater</td>
<td>1 \times 10^{-6}</td>
<td>17.0</td>
<td>1 \times 10^{-3}</td>
</tr>
<tr>
<td>Baking soda</td>
<td>1 \times 10^{-7}</td>
<td>18.0</td>
<td>1 \times 10^{-2}</td>
</tr>
<tr>
<td>Borax</td>
<td>1 \times 10^{-8}</td>
<td>19.0</td>
<td>1 \times 10^{-1}</td>
</tr>
<tr>
<td>Milk of magnesia</td>
<td>1 \times 10^{-9}</td>
<td>20.0</td>
<td>1 \times 10^0</td>
</tr>
<tr>
<td>Lime water</td>
<td>1 \times 10^{-10}</td>
<td>21.0</td>
<td>1 \times 10^1</td>
</tr>
<tr>
<td>Household ammonia</td>
<td>1 \times 10^{-11}</td>
<td>22.0</td>
<td>1 \times 10^2</td>
</tr>
<tr>
<td>Household bleach</td>
<td>1 \times 10^{-12}</td>
<td>23.0</td>
<td>1 \times 10^3</td>
</tr>
<tr>
<td>NaOH, 0.1 M</td>
<td>1 \times 10^{-13}</td>
<td>24.0</td>
<td>1 \times 10^4</td>
</tr>
</tbody>
</table>
| pH and pOH for selected substance (Brown LeMay)

Relating \([H_3O^+], [OH^-], \text{pH and pOH}\)

**Example**: the pH of rain water was measured to be 4.35 whilst that of aqueous ammonia was found to be 11.28. Determine \([H_3O^+]\) in water and \([OH^-]\) in ammonia.

**Acid and Base Strength**

In any acid-base reaction, the equilibrium will favour the reaction that moves the proton to the stronger base.

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

\(\text{H}_2\text{O}\) is a much stronger base than \(\text{Cl}^-\), so the equilibrium lies so far to the right \(K\) is not measured \((K>>1)\).

We can easily calculate the pH of aqueous solutions of **strong** mono protic acids such as HCl, HBr, HI, HNO₃, HClO₄ because they are essentially fully ionized and thus a 1M HNO₃ will ionize to give 1M H⁺.

**Example**: Calculate the pH of a 0.0025 M HCl
Example: What is the proton ion concentration of a solution that has a pH of 4.5

What about the pH of weak acids like acetic acid or HF and what about acids that can give off more than one hydrogen ion upon ionization H₃PO₄, H₂SO₄?

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+
\]

Acetate is a stronger base than H₂O, so the equilibrium favours the left side (K < 1).

**Dissociation Constants**

- For a generalized acid dissociation,

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

  The equilibrium expression would be: \( K_a = \frac{[A^-][H^+]}{[HA]} \)

  **This equilibrium constant is called the acid-dissociation constant, \( K_a \).**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structural Formula</th>
<th>Conjugate Base</th>
<th>Equilibrium Reaction</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrofluoric (HF)</td>
<td>F^-</td>
<td>HF(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + F^-(aq)</td>
<td>6.8 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Nitrous (HNO₂)</td>
<td>NO₂^-</td>
<td>HNO₂(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + NO₂^-(aq)</td>
<td>4.5 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Benzonic (H₂C₄O₄)</td>
<td>C₂H₄O₂^-</td>
<td>C₂H₄O₂⁻(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + C₂H₄O₂⁻(aq)</td>
<td>6.3 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>Acetic (H₃C₂O₄)</td>
<td>C₂H₃O₂^-</td>
<td>C₂H₃O₂⁻(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + C₂H₃O₂⁻(aq)</td>
<td>6.3 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>Hypochlorous (HClO)</td>
<td>ClO^-</td>
<td>ClO⁻(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + ClO⁻(aq)</td>
<td>3.0 \times 10^{-8}</td>
<td></td>
</tr>
<tr>
<td>Hydronycyanic (HCN)</td>
<td>CN^-</td>
<td>HCN⁻(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + CN⁻(aq)</td>
<td>4.9 \times 10^{-10}</td>
<td></td>
</tr>
<tr>
<td>Phenol (H₃C₆H₅O)</td>
<td>C₆H₅O^-</td>
<td>C₆H₅O⁻(aq) + H₂O(l) \rightleftharpoons H₂O^+(aq) + C₆H₅O⁻(aq)</td>
<td>1.3 \times 10^{-10}</td>
<td></td>
</tr>
</tbody>
</table>

\*The proton that tautomerizes is shown in blue.

**pH of weak acids:**

Example: What is the pH of a 0.100 M acetic acid solution:

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+
\]

Initial conc.: \( 0.1000 \text{M} \)

Change: \(-x \text{ M}, +x \text{ M}, +x \text{ M}\)

Equilibrium: \( (0.100 - x) \text{M} \)

We also know the acid dissociation constant \( K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{\text{CH}_3\text{COOH}} = \frac{x^2}{0.1-x} \)