ACID-BASE EQUILIBRIUM

Concept of Acid/Base

The earliest definition for acids are substances which dissociated in water to produce hydrogen ions:

\[ \text{e.g. } \ HCl \rightarrow H^+ + Cl^- \]

Since it is impossible for such a small and high charge ion like \( H^+ \) to exist independently in aqueous solutions, \( H^+ \) ions were believed to associate with polar water molecules to exist in the form of \( H_3O^+ \), known as hydronium ions:

\[ \text{H}^+ + H_2O \rightarrow H_3O^+ \]

making the dissociation of acids in water represented more accurately as:

\[ \text{HCl} (aq) + H_2O(l) \rightarrow H_3O^+ (aq) + Cl^- (aq) \]

Weak acids which are only partially dissociated can thus be represented as:

\[ \text{CH}_3\text{COOH} (aq) + H_2O(l) \leftrightarrow H_3O^+ (aq) + \text{CH}_3\text{COO}^- (aq) \]

Notice that
1. it explains why substances such as hydrogen chloride and ethanoic acid only show their acidic properties in the presence of water
2. such ionic equilibrium is in many ways similar to redox equilibrium:

<table>
<thead>
<tr>
<th>Acid-base equilibrium</th>
<th>Redox equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{COOH} + H_2O \leftrightarrow H_3O^+ + \text{CH}_3\text{COO}^- )</td>
<td>( \text{Fe}^{2+} (aq) + \text{Zn} (s) \leftrightarrow \text{Fe} (s) + \text{Zn}^{2+} (aq) )</td>
</tr>
<tr>
<td>Acid base conjugate conjugate</td>
<td>oxidant reductant reductant oxidant</td>
</tr>
<tr>
<td>depends on the relative strength of acids</td>
<td>which depends on the relative position in the ECS</td>
</tr>
<tr>
<td>transfer of protons are taking place</td>
<td>transfer of electrons are taking place</td>
</tr>
<tr>
<td>an acid, after reaction, will become its conjugate base (and vice versa)</td>
<td>an oxidizing agent, after reaction, will become a reducing agent (and vice versa)</td>
</tr>
<tr>
<td>the stronger the acid, the weaker its conjugate base (and vice versa) ⇒ conjugate theory</td>
<td>the stronger the oxidant, the weaker its &quot;conjugate&quot; reductant (and vice versa)</td>
</tr>
</tbody>
</table>

Hence, the concept of acids and bases is best summarized by the Bronsted-Lowry theory, which states that:

An acid is a proton donor.
A base is a proton acceptor.

Class Work

(a) What is the conjugate acid of
   (i) \( \text{CH}_3\text{COO}^- \)
   (ii) \( \text{HSO}_4^- \)
   (iii) \( \text{NH}_3 \)
   (iv) \( \text{OH}^- \) ?

(b) What is the conjugate base of
   (i) \( \text{HNO}_3 \)
   (ii) \( \text{HCO}_3^- \)
   (iii) \( \text{HSO}_4^- \)
   (iii) \( \text{NH}_3 \) ?

(c) Write equations to show that nitric(V) acid is an acid in water, but a base in liquid hydrogen fluoride.

Calculations of \( pH \) for Strong Acids and Bases

\( pH \) scale is a universal measure of acidity based on the concentration of hydrogen ions:

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

\( \therefore \) the stronger an acid, the lower its \( pH \) value
Acid 2

Pure water has a tiny electrical conductivity, owing to the slight dissociation of water molecules into ions:

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

The equilibrium position in this reaction lies far to the left. Nevertheless, we can write an equilibrium constant, specifically known as the ionic product of water \((K_w)\), for the dissociation of water as:

\[
K_w = [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol dm}^{-6} \text{ at } 25^\circ\text{C}
\]

It follows that at 25°C:
- neutral medium \([\text{H}^+] = [\text{OH}^-]\) \(\text{pH} = 7\)
- acidic medium \([\text{H}^+] > [\text{OH}^-]\) \(\text{pH} < 7\)
- alkaline medium \([\text{H}^+] < [\text{OH}^-]\) \(\text{pH} > 7\)

The dissociation of water is an endothermic process:

\[ \text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad \Delta H = +58 \text{ kJ mol}^{-1} \]

Increase in temperature ⇒ the equilibrium shifts to the right
⇒ \([\text{H}^+(aq)]\) increases
⇒ pH of pure water at temperature higher than 25°C is less than 7.0

**Class Work**
Calculate the pH value for each of the following solutions:
(a) 0.1 M HCl
(b) 0.1 M H\(_2\)SO\(_4\)
(c) 0.1 M NaOH
(d) \(10^{-9}\) M HCl
(e) 10 M HCl

**Calculations of pH for Weak Acids and Bases**

For a weak acid HA:

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

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

where \(K_a\) is the dissociation constant for a weak acid, with its value differs from one weak acid to another.

**Class Work**
Calculate the pH value for each of the following solutions:
(a) 0.1 M CH\(_3\)COOH \((K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3})\)
For a weak base $B$:

\[ B(aq) + H_2O(l) \rightleftharpoons HB^-(aq) + OH^-(aq) \]

where $K_b$ is the dissociation constant for a weak base.

**Class Work**

(a) Calculate the pH value of a 0.5 M solution of ammonia, given $K_b$ of ammonia is $1.8 \times 10^{-5}$ mol dm$^{-3}$.

(b) Determine the dissociation constant, $K_a$, of ammonium ion $NH_4^+$. Notice that:

1. The magnitude of $K_a$ and $K_b$ gives indirect measure of the acidic (or basic) strength of weak acids (or bases)
   
   - $K_a$ or $pK_a$ increases, $K_b$ or $pK_b$ decreases, stronger acid
   
   - $K_a$ or $pK_a$ decreases, $K_b$ or $pK_b$ increases, stronger base

2. The larger $K_a$ value of a weak acid, the smaller $K_b$ value its conjugate base would be (and vice versa)

   - $K_a \times K_b = K_w$

**Buffer Solutions**

Buffers are solutions which resists changes in pH on addition of small amount of acid or alkali.

**Class Work**

(a) Calculate the change in pH when 0.1 cm$^3$ of 1.0 M HCl is added to 1 dm$^3$ of pure water at 298 K.

(b) Calculate the pH of the resulting solution when 300 cm$^3$ 0.1 M CH$_3$COOH is mixed with 100 cm$^3$ 0.1 M CH$_3$COONa.
Underlying Principle of Buffering Action

Buffer solutions usually consist of:

1. **either** a solution of a weak acid in the presence of one of its salts (i.e. conjugate bases);
2. **or** a solution of a weak base in the presence of one of its salts (i.e. conjugate acids).

In order to understand how a buffer works, we can consider the hypothetical weak acid, HA, in a solution with its salt MA. In this solution, HA will be slightly ionized, whereas MA is fully dissociated:

\[
\begin{align*}
HA & \leftrightarrow H^+ + A^- \\
MA & \rightarrow M^+ + A^- 
\end{align*}
\]

Hence the mixture contains both the ionized A⁻ and the unionized HA in relatively high concentrations.

If acid is suddenly added to this system
= equilibrium will shift to the left
\Rightarrow H^+ ions in the acid will combine with A⁻ ions in the buffer to form the unionized HA, reducing its concentration in the buffer.

If base is suddenly added to this system
\Rightarrow OH⁻ ions from the base combine with H⁺ ions, equilibrium will shift to the right, more HA dissociates to restore [H⁺] to its original value.

Provided there is a large reservoir of A⁻ ions and unionized HA in the buffer, [H⁺] changes very little and the pH is only slightly altered. \( \therefore \) **buffering capacity of a solution increases with its concentration.**

Calculation of pH of Buffer Solutions

We can write an expression for the dissociation constant of HA as:

\[
K_a = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [H^+] = K_a \times \frac{[HA]}{[A^-]}
\]

In the buffer mixture: 
- [HA] \( \equiv \) [acid] (the weak acid, HA, is only slightly dissociated)
- [A⁻] \( \equiv \) [salt] (the salt, MA, is fully dissociated)

Therefore:

\[
[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}
\]

Notice that:

1. **the pH of a buffer is governed by the ratio** \( \frac{[\text{acid}]}{[\text{salt}]} \) (or \( \frac{[HA]}{[A^-]} \))
2. **the pH of a buffer is affected very little by dilution, because the ratio** \( \frac{[\text{acid}]}{[\text{salt}]} \) will remain constant on dilution
3. **when** \( [\text{acid}] = [\text{salt}] \) \( \Rightarrow \) **[H⁺] = K_a**

such special case provides a convenient way to **determine** \( K_a \) of any weak acid simply by measuring its pH when the condition \( [\text{acid}] = [\text{salt}] \) is valid (i.e. when the acid is **half-neutralized**)

Class Work

Determine the change in pH if each of the following is added to the solution in the previous class work on p.3:

(a) 1 cm³ of 1.0 M HCl is added

(b) 0.001 mole NaOH is added
In what proportion will the following pairs of solutions be mixed in order to obtain the buffer with the corresponding pH:

(a) 0.1 M CH₃COOH  }  100 cm³ solution with pH = 5  (Kₐ of CH₃COOH = 1.8 x 10⁻⁵ M)
     0.1 M CH₃COONa

(b) 1.0 M NH₃  }  1 dm³ solution with pH = 9  (Kₐ of NH₃ = 1.8 x 10⁻⁵ M)
     1.0 M NH₄Cl

Buffers are mainly used:
1 in the laboratory (i) to prepare solutions of known and constant pH; and (ii) to calibrate pH meters
2 in living organisms to maintain optimal metabolic activities (e.g. buffer systems are essential in maintaining an almost constant pH value at about 7.4 in the blood of healthy human bodies)

**Acid-base Indicators**

Acid-base indicators are substances which change colour according to the hydrogen ion concentration of the solution to which they are added. Most indicators can be regarded as weak acids of which either the undissociated molecule, HIn, or the dissociated anion, In⁻, or both, are coloured:

\[
\text{HIn} \leftrightarrow \text{H}^+ + \text{In}^-
\]

methyl orange
phenolphthalein

The colour of any indicator depends on the relative concentrations of the acidic form, HIn, and the alkaline form, In⁻, which are of different colours.

**Class Work**

A few drops of methyl orange indicator is added to a series of buffer solutions ranging from pH 2 to 7. Determine its colour at different pH. (Given Kₐ of methyl orange is 10⁻⁴ mol dm⁻³)

<table>
<thead>
<tr>
<th>pH</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\frac{[\text{In}^-]}{[\text{HIn}]^}]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
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<tr>
<td>observed colour</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
<td>[ ]</td>
</tr>
</tbody>
</table>

Notice that:
1 It is impossible to say precisely when the two forms are at equal concentrations. Experience shows that our eyes cannot judge the exact point at which the colour changes, and indicators effectively change colour over a working range of about 2 pH units.
2 The dissociation constant for different acid-base indicators are different. Therefore, they change colour over different pH ranges. In general, the working range of any indicator is related to its dissociation constant by:

\[
\text{working range} = pK_a + 1
\]
**Acid-base Titrations**

During a titration there is a change in pH as alkali is added to acid or vice versa. At the equivalence point, the pH must change sharply by several units for it to be identified by an acid-base indicator.

**pH Titration Curves**

The change in pH during the course of a titration depends largely upon the strength of the acid and alkali used.

**Case I - Strong Acid vs. Strong Base**

HCl(aq) + NaOH(aq) → NaCl(aq) + H₂O(l)

25 cm³ of 0.1 M HCl solution in a conical flask is going to be titrated by 0.1 M NaOH solution. Plot the titration curve by calculating the corresponding pH value as shown in the following table:

<table>
<thead>
<tr>
<th>volume of 0.1 M NaOH added / cm³</th>
<th>0.0</th>
<th>5.0</th>
<th>10.0</th>
<th>20.0</th>
<th>24.5</th>
<th>24.9</th>
<th>25.0</th>
<th>25.1</th>
<th>25.5</th>
<th>30.0</th>
<th>35.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount of HCl remained / mol.</td>
<td></td>
<td></td>
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<tr>
<td>total volume / cm³</td>
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</tr>
<tr>
<td>[H⁺]</td>
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<tr>
<td>pH</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Indicator</th>
<th>“Acid”</th>
<th>“Base”</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl orange</td>
<td>red</td>
<td>yellow</td>
<td>3.2 – 4.4</td>
</tr>
<tr>
<td>methyl red</td>
<td>yellow</td>
<td>red</td>
<td>4.8 – 6.0</td>
</tr>
<tr>
<td>bromothymol blue</td>
<td>yellow</td>
<td>blue</td>
<td>6.0 – 7.6</td>
</tr>
<tr>
<td>phenol red</td>
<td>yellow</td>
<td>red</td>
<td>6.8 – 8.4</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>colorless</td>
<td>pink</td>
<td>8.2 – 10.0</td>
</tr>
</tbody>
</table>

**Diagram:**

- pH vs. volume of NaOH added (cm³) graphs.
$Case II - Weak Acid vs. Strong Base$  

$$HA_{(aq)} + NaOH_{(aq)} \rightarrow Na^+_{(aq)} + A^-_{(aq)} + H_2O_{(l)}$$

25 cm$^3$ of 0.1 M solution of acetylsalicylic acid (aspirin) in a conical flask is going to be titrated by 0.1 M NaOH solution. Plot the titration curve by completing the following table: (given that $K_a$ for acetylsalicylic acid = $3 \times 10^{-4}$ mol dm$^{-3}$)

<table>
<thead>
<tr>
<th>volume of 0.1 M NaOH added (cm$^3$)</th>
<th>0.0</th>
<th>5.0</th>
<th>10.0</th>
<th>20.0</th>
<th>24.5</th>
<th>24.9</th>
<th>25.0</th>
<th>25.5</th>
<th>30.0</th>
<th>35.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HA]</td>
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<tr>
<td>[A$^-$]</td>
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<tr>
<td>pH</td>
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</tbody>
</table>

Sketch the pH titration curves for the following cases, based upon the shape of the above two:

$Case III - Strong Acid vs. Weak Base$  $Case IV - Weak Acid vs. Weak Base$

### Choices of Indicators

Generally speaking, if a visual indicator is to be used to determine the end-point of an acid-base titration, its pH working range should fall on the ‘vertical portion’ of the titration curve, making the theoretical equivalence point (the point in a titration where the amount of acid equals the amount of base) coincides with the experimental end-point (the point in a titration where a particular indicator changes colour).

Notice that:

1. There is no suitable indicator for the titration involving weak acids and weak bases, because:
   - the change in pH in the ‘vertical portion’ of such titration curve is not sharp enough; and
   - all acid-base indicators change their colours within a range instead of a single value

2. The end-point of a titration may not necessarily be neutral (i.e. pH = 7), depending on whether the salt formed in the titration undergoes hydrolysis or not

3. The end-point of a titration can be determined by other physical methods without using acid-base indicators:
   - **thermometric** titration (to monitor the variation in temperature)
     - temp. begins to rise before the end-point is reached
     - rise in temp. is maximum during the end-point
     - temp. begins to fall after the end-point is reached
     - no further neutralization + cooling effect
   - **conductometric** titration (to monitor the variation in conductivity)
     - conductivity decreases before the end-point is reached
     - conductivity increases after the end-point is reached
     - slope after the end-point is less steeper than that before the end-point

<table>
<thead>
<tr>
<th>type of titration</th>
<th>appropriate indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid</td>
<td>base</td>
</tr>
<tr>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>weak</td>
<td>strong</td>
</tr>
<tr>
<td>weak</td>
<td>strong</td>
</tr>
</tbody>
</table>

- temp. begins to rise before the end-point is reached
- conductivity decreases before the end-point is reached
- conductivity increases after the end-point is reached
- slope after the end-point is less steeper than that before the end-point
- OH$^-$ ions are less mobile than H$^+$ ions
**Salt Hydrolysis**

In pure water, the concentrations of $H^+$ ions and $OH^-$ ions are the same. Certain salts, however, can disturb this balance when they are dissolved in water, the phenomenon of which is known as **hydrolysis**. Whether a salt would be hydrolyzed or not depends on the strength of the parent acid and base where the salt is produced from:

1. salts formed from strong acids and strong bases (e.g. NaCl):
   
   \[ \text{NaCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) + \text{H}^+(aq) + \text{Cl}^-(aq) \quad \text{i.e. no reaction} \]
   
   \[ [H^+] = [OH^-] \quad \Rightarrow \quad \text{salt is neutral} \]

2. salts formed from weak acids and strong bases (e.g. \( \text{CH}_3\text{COONa} \)):

   \[ \text{CH}_3\text{COONa(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) + \text{CH}_3\text{COOH(aq)} \]
   
   \[ [H^+] < [OH^-] \quad \Rightarrow \quad \text{salt is alkaline} \]

3. salts formed from strong acids and weak bases (e.g. \( \text{NH}_4\text{Cl} \)):

   \[ \text{NH}_4\text{Cl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{NH}_3(aq) + \text{H}_2\text{O(l)} + \text{H}^+(aq) + \text{Cl}^-(aq) \]
   
   \[ [H^+] > [OH^-] \quad \Rightarrow \quad \text{salt is acidic} \]

**Class Work**

(a) Decide whether each of the following salts is acidic, alkaline or neutral:

(i) \( \text{Na}_2\text{SO}_4 \)  
(ii) \( \text{FeCl}_3 \)  
(iii) \( \text{KNO}_3 \)

(iv) \( \text{NaHCO}_3 \)  
(v) \( \text{NaHSO}_4 \)

(b) Calculate the pH value of a 0.1 M solution of sodium ethanoate, \( \text{CH}_3\text{COONa} \).

(Given that \( K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \); \( K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \))
**Solubility Product**

Consider the dissolution of a *sparingly* soluble salt MX (e.g. AgCl) in water:

$$MX(s) = M^+(aq) + X^-(aq)$$

When a saturated solution is formed in the presence of excess salt MX(s), a dynamic equilibrium exists when the rate of dissolution (ie. forward rxn) is equal to the rate of precipitate formation (backward rxn). The constant of the above heterogeneous equilibrium is expressed as:

$$K_c = \frac{[M^+(aq)] [X^-(aq)]}{[MX(s)]}$$

For heterogeneous equilibria:

$$[MX(s)] = \text{constant}$$

By incorporating $[MX(s)]$ into $K_c$, a new constant known as the **solubility product**, $K_{sp}$, is defined as:

$$K_{sp} = [M^+(aq)] [X^-(aq)]$$

Notice that:

1. The solubility product for a given salt is a constant at a given temperature.
2. It is assumed that the salt does not undergo any hydrolysis during solvation.
3. $K_{sp}$ shows the maximum value of the ionic product of $M^+(aq)$ and $X^-(aq)$ ions that can exist in a *saturated* solution without formation of precipitate. There are three possible cases when the ionic product (reaction quotient) is compared with $K_{sp}$:
   
   a. $Q < K_{sp}$: solution is not saturated and more salt can be dissolved in it
   b. $Q = K_{sp}$: a saturated solution is formed & the system is at equilibrium
   c. $Q > K_{sp}$: solution is supersaturated; precipitate will be formed until ionic product restores to the $K_{sp}$ value

Hence, it provides a useful measure of **solubility**: if conditions alter such that the ionic product exceeds the $K_{sp}$ value at a given temperature, MX(s) would be precipitated until the ionic product restores to the $K_{sp}$ value.

While **solubility product** is an *equilibrium constant* and has only one value for a given salt at a particular temperature, **solubility** refers to the equilibrium amount of solute dissolved in a certain volume of saturated solution, which is related to the *equilibrium position* and can have infinite number of possible values at a given temperature, depending on many other conditions. Nevertheless, solubility can be calculated from $K_{sp}$ and vice versa.

**Class Work**

(a) Calculate the solubility product of the following salts, given their corresponding solubility quoted in brackets:

(i) $\text{AgCl} \ (1.4 \times 10^{-5} \text{ mol dm}^{-3})$
(ii) $\text{PbI}_2 \ (0.55 \text{ g dm}^{-3})$ [Pb: 207; I: 127]

(b) Calculate the solubility of the following salts, given their corresponding solubility products quoted in brackets:

(i) $\text{PbSO}_4 \ (K_{sp} = 1.6 \times 10^{-8})$
(ii) $\text{Ag}_2\text{SO}_4 \ (K_{sp} = 1.6 \times 10^{-5})$

(c) A mixture solution containing 0.01M $\text{Pb}^{2+}$ and 0.01M $\text{Ag}^+$ is added to an equal volume of 0.1 M Na$_2$SO$_4$ solution. Predict which ion will be precipitated first.
Devise an experiment to determine the solubility product of silver chloride, making use of a piece of copper wire. Outline the experimental procedure and data treatment involved.

According to Le Chatelier’s principle, addition of a common ion [M⁺(aq) or X⁻(aq)] will shift the above equilibrium position to the left, leading to the formation of more precipitate or, in other words, reducing the solubility of the salt. Such common ion effect has a wide range of applications in daily life, including the ‘salting out’ process (ie. addition of saturated NaCl solution) in the manufacture of soap.

Calculate the solubility of Ca(OH)₂ in each of the following cases, given that its solubility product is $6.5 \times 10^{-6}$ mol$^3$ dm$^{-9}$:

(a) pure water
(b) 0.1 M NaOH(aq)