(1) Concept of acid / base

The best definition of acids and bases is that proposed by T.M. Lowry and also, independently by J.N. Bronsted in 1923.

Bronsted-Lowry theory

1. According to Bronsted-Lowry, acid is proton (H⁺) donor and base is proton acceptor.

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

acid \hspace{1cm} conjugate base

Every acid has a conjugate base and every base has a conjugate acid. When a Bronsted-Lowry acid loses a proton, it becomes the conjugate base of the acid. When a base accepts a proton, it becomes the conjugate acid of the base.

Example 1

When hydrogen chloride is dissolved in water, each HCl molecule donates a proton to a water molecule and acts as Bronsted-Lowry acid. Each water acts as a Bronsted-Lowry base when it accepts a proton from the acid, forming a hydroxonium ion.

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

acid 1 \hspace{1cm} base 2 \hspace{1cm} conjugate base 1 \hspace{1cm} conjugate acid 2

Cl⁻_{(aq)} is the remains of the acid molecule HCl_{(aq)} after the proton is lost, and is called the conjugate base of HCl_{(aq)}. Hydroxonium ion, H₃O⁺_{(aq)}, is formed when the proton is transferred to the base H₂O_{(l)}, and is called the conjugate acid of H₂O_{(l)}.

2. For an acid to behave as an acid, it is necessary to have a base to accept the proton. Therefore, an acid only shows acidic properties in the presence of a base.

Example 2

\[
\begin{align*}
\text{CH}_3\text{COOH}_{(aq)} + & \text{H}_2\text{O}_{(l)} \rightarrow \text{CH}_3\text{COO}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \\
\text{H}_2\text{SO}_4_{(aq)} + & \text{H}_2\text{O}_{(l)} \rightarrow \text{HSO}_4^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \\
\text{HSO}_4^-_{(aq)} + & \text{H}_2\text{O}_{(l)} \rightarrow \\
\text{HCO}_3^-_{(aq)} + & \text{H}_2\text{O}_{(l)} \rightarrow 
\end{align*}
\]

3. For a base to behave as a base, it is necessary to have an acid to donate the proton. Therefore, a base only shows basic properties in the presence of an acid.

Example 3

\[
\begin{align*}
\text{H}_2\text{O}_{(l)} + & \text{CH}_3\text{COO}^-_{(aq)} \\
\text{H}_2\text{O}_{(l)} + & \text{NH}_3_{(aq)} \\
\text{H}_2\text{O}_{(l)} + & \text{CN}^-_{(aq)} \\
\text{H}_2\text{O}_{(l)} + & \text{HCO}_3^-_{(aq)}
\end{align*}
\]
4. **Amphoteric substance** is a chemical species which can behave as a Bronsted-Lowry acid or base, depending on the substance it react with. For example, water is amphoteric because it acts as a base and an acid when it reacts with HCl\(_{(aq)}\) and NH\(_3\)\(_{(aq)}\) respectively. HCO\(_3\)\(^-\)\(_{(aq)}\) is also an amphoteric species, it can donate or accept a proton when reacts with water.

\[
\begin{align*}
\text{H}_2\text{CO}_3\text{(aq)} & \quad \text{HCO}_3\text{\(^-\)}\text{(aq)} & \quad \text{CO}_3\text{\(^{2-}\)}\text{(aq)} \\
\text{H}^+\text{(aq)} & \quad \text{H}^+\text{(aq)} \\
\text{accepts proton, acts as a Bronsted base} & \quad \text{donates proton, acts as a Bronsted acid}
\end{align*}
\]

5. According to Bronsted-Lowry, a reaction between an acid and a base is a **proton transfer reaction** that involves two conjugate acid-base pairs.

**Example 4**

In each of the following reactions one of the reactants is behaving as a base. In each case underline the species you believe to be the base.

(a) \(\text{H}_2\text{PO}_4\text{\(^-\)}\text{(aq)} + \text{HCO}_3\text{\(^-\)}\text{(aq)} \rightleftharpoons \text{HPO}_4\text{\(^{2-}\)}\text{(aq)} + \text{H}_2\text{CO}_3\text{(aq)}\)

(b) \(\text{HBr\(_(l)\)} + \text{HCl\(_(l)\)} \rightleftharpoons \text{Br}^-\text{(l)} + \text{H}_2\text{Cl}^+\text{(l)}\)

(c) \(\text{HNO}_3\text{(l)} + \text{HClO}_4\text{(l)} \rightleftharpoons \text{H}_2\text{NO}_3\text{\(^+\)}\text{(l)} + \text{ClO}_4\text{\(^-\)}\text{(l)}\)

**Example 5**

Write equation to show that NH\(_4\text{\(^+\)}\text{(aq)}\) can act as a Bronsted acid in water.

**Example 6**

Write equation to show that CO\(_3\text{\(^{2-}\)}\text{(aq)}\) can act as a Bronsted base in water.

**Example 7**

Write equations to show that HPO\(_4\text{\(^{2-}\)}\text{(aq)}\) can act as a Bronsted acid or a Bronsted base in water.

**Example 8**

Write equations to show that nitric(V) acid is an acid in water, but a base in liquid hydrogen fluoride.
(2) Dissociation of water and pH

1. Dissociation of water

According to Bronsted-Lowry theory, water can act as both an acid and a base because it can self-ionize:

\[
\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

The equilibrium constant is

\[
K_c = \frac{[\text{H}_3\text{O}^+(aq)][\text{OH}^-(aq)]}{[\text{H}_2\text{O}(l)]^2}
\]

Since a very small fraction of water is dissociated, \([\text{H}_2\text{O}(l)]\) is almost constant.

\[
K_c \times [\text{H}_2\text{O}(l)]^2 = Kw = [\text{H}_3\text{O}^+(aq)][\text{OH}^-(aq)]
\]

**Kw is the ionic product of water.** Its value depends on temperature. When temperature increases, Kw increases.

It is important to recognize the meaning of Kw. In any aqueous solution at 25°C, the product of \([\text{H}_3\text{O}^+(aq)]\) and \([\text{OH}^-(aq)]\) must always equal to \(1.00 \times 10^{-14}\) mol\(^2\) dm\(^{-6}\). There are three possible situations:

(1) A neutral solution, where \([\text{H}_3\text{O}^+(aq)] = [\text{OH}^-(aq)]\)

(2) An acidic solution, where \([\text{H}_3\text{O}^+(aq)] > [\text{OH}^-(aq)]\)

(3) A basic solution, where \([\text{H}_3\text{O}^+(aq)] < [\text{OH}^-(aq)]\)

Example

Given that:

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Kw / mol(^2) dm(^{−6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.29 \times 10^{-14}</td>
</tr>
<tr>
<td>20</td>
<td>0.68 \times 10^{-14}</td>
</tr>
<tr>
<td>25</td>
<td>1.00 \times 10^{-14}</td>
</tr>
<tr>
<td>30</td>
<td>1.47 \times 10^{-14}</td>
</tr>
<tr>
<td>40</td>
<td>2.92 \times 10^{-14}</td>
</tr>
</tbody>
</table>

(a) Is the dissociation of water into ions an exothermic or an endothermic process?

It is an endothermic process. According to Le Chatelier’s principle, an increase in temperature will increase the equilibrium constant for an endothermic reaction.

(b) Calculate the concentration of hydroxonium ions for pure water at 25°C and 40°C.

Note that:

**Hydroxonium ion, H\(_3\)O\(^+\)(aq), is often simplified as hydrogen ion, H\(^+\)(aq).**
2. **pH and its measurement**

The pH of a solution is the negative of the logarithm to base 10 of its hydroxonium ion concentration.

\[ \text{pH} = -\log_{10} [\text{H}_3\text{O}^+_{\text{aq}}] \]

Also,

\[ \text{pOH} = -\log_{10} [\text{OH}^-_{\text{aq}}] \]

Since at 25 °C, in any aqueous solution, \( K_w = [\text{H}_3\text{O}^+_{\text{aq}}] [\text{OH}^-_{\text{aq}}] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \)

\[ \text{pH} + \text{pOH} = 14.0 \]

Note that:

(1) a neutral solution, where \([\text{H}_3\text{O}^+_{\text{aq}}] = [\text{OH}^-_{\text{aq}}] = 10^{-7} \text{ mol dm}^{-3} \Rightarrow \text{pH} = 7.

(2) an acidic solution, where \([\text{H}_3\text{O}^+_{\text{aq}}] > [\text{OH}^-_{\text{aq}}] \Rightarrow \text{pH} < 7.

(3) a basic solution, where \([\text{H}_3\text{O}^+_{\text{aq}}] < [\text{OH}^-_{\text{aq}}] \Rightarrow \text{pH} > 7.

Since pH is a log scale based on 10, the pH changes by 1 unit for every ten-fold change in \([\text{H}_3\text{O}^+_{\text{aq}}].\)

<table>
<thead>
<tr>
<th>Concentration of HCl(_{\text{aq}})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M</td>
<td>1</td>
</tr>
<tr>
<td>0.01M</td>
<td>2</td>
</tr>
<tr>
<td>0.001M</td>
<td>3</td>
</tr>
<tr>
<td>0.0001M</td>
<td>4</td>
</tr>
</tbody>
</table>

**Example 1**

(a) Calculate the hydroxide ion concentration in 0.10 mol dm\(^{-3}\) hydrochloric acid.

As HCl\(_{\text{aq}}\) is a strong acid, \([\text{H}^+_{\text{aq}}] = 0.10 \text{ mol dm}^{-3}.\)

\([\text{H}^+_{\text{aq}}][\text{OH}^-_{\text{aq}}] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \]

\([\text{OH}^-_{\text{aq}}] = 1.00 \times 10^{-13} \text{ mol dm}^{-3} \]

(b) Calculate the hydrogen ion concentration and pH value of 0.010 mol dm\(^{-3}\) calcium hydroxide solution.

\([\text{OH}^-_{\text{aq}}] = 0.020 \text{ mol dm}^{-3} \] as 0.010 M Ca(OH)\(_2_{\text{aq}}\) dissolves.

\([\text{H}^+_{\text{aq}}][\text{OH}^-_{\text{aq}}] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \]

\([\text{H}^+_{\text{aq}}] = 5.00 \times 10^{-13} \text{ mol dm}^{-3} \]

\(\text{pH} = 12.3 \]

(c) Calculate the pH of 0.010 mol dm\(^{-3}\) sulphuric acid.

**Example 2**

(a) Calculate the concentration of an aqueous solution of nitric acid whose pH = 1.7

(b) Calculate the pH of a solution resulting from the addition of 32.0 cm\(^3\) of 0.0010 mol dm\(^{-3}\) sodium hydroxide to 50.0 cm\(^3\) of 0.0010 mol dm\(^{-3}\) hydrochloric acid.

Number of moles of H\(^+\)\(_{\text{aq}}\) remained after neutralization =
Use of indicators to measure pH

There is a range of naturally occurring dyes whose colours are affected by the concentration of hydroxonium ions present. These substances are called indicators and their colours and colour changes give some guide to the pH of the solution into which they are added.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>PH 1</th>
<th>PH 2</th>
<th>PH 3</th>
<th>PH 4</th>
<th>PH 5</th>
<th>PH 6</th>
<th>PH 7</th>
<th>PH 8</th>
<th>PH 9</th>
<th>PH 10</th>
<th>PH 11</th>
<th>PH 12</th>
<th>PH 13</th>
<th>PH 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>red</td>
<td>orange</td>
<td>yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Litmus</td>
<td>red</td>
<td>red-blue</td>
<td>blue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>colourless</td>
<td>pink</td>
<td>red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Universal</td>
<td>red</td>
<td>orange</td>
<td>yellow</td>
<td>green</td>
<td>blue</td>
<td>violet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Use of pH meter to measure pH

A pH meter is an electrochemical cell consisting of 2 electrodes: a reference electrode with constant electrode potential and a glass electrode sensitive to hydrogen ion concentration.

The pH meter should be calibrated before use:
1. Rinse the electrode with distilled water.
2. Dip the electrode into buffers of known pH values.
3. Adjust the pH meter so that its reading agrees with the pH of the buffer.
4. Rinse the electrode with distilled water again.

To measure the pH value of a solution, the calibrated pH meter is immersed in the solution and the pH value can be read.
(3) Strong and weak acids / bases

1. Dissociation constants for weak acids (Ka) and weak bases (Kb)

An equilibrium is set up when an acid is added to water:

$$\text{HA}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{A}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$$

The equilibrium constant $K_c$ is given by the expression:

$$K_c = \frac{[\text{A}^-_{(aq)}][\text{H}_3\text{O}^+_{(aq)}]}{[\text{HA}_{(aq)}][\text{H}_2\text{O}_{(l)}]}$$

The value of $[\text{H}_2\text{O}_{(l)}]$ is always 55.6 mol dm$^{-3}$. When this value is put into the equilibrium expression, a new equilibrium constant $K_a$ is obtained:

$$K_c \times [\text{H}_2\text{O}_{(l)}] = K_a = \frac{[\text{A}^-_{(aq)}][\text{H}_3\text{O}^+_{(aq)}]}{[\text{HA}_{(aq)}]}$$

$K_a$ is called the dissociation constant for the acid HA.

For a strong acid, $K_a$ is large. The equilibrium position for the dissociation lies far to the right. Dissociation of $\text{HA}_{(aq)}$ into $\text{H}_3\text{O}^+_{(aq)}$ and $\text{A}^-_{(aq)}$ is assumed to be complete. The equilibrium concentration of $\text{H}_3\text{O}^+_{(aq)}$ is close to the original concentration of $\text{HA}_{(aq)}$.

For a weak acid, $K_a$ is small. The equilibrium position for the dissociation lies far to the left. $\text{HA}_{(aq)}$ is only partially dissociated into $\text{H}_3\text{O}^+_{(aq)}$ and $\text{A}^-_{(aq)}$. Most of the acid still exists as undissociated molecules at equilibrium.

A similar expression can be derived for the equilibrium condition of a weak base in water:

$$\text{B}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{BH}^+_{(aq)} + \text{OH}^-_{(aq)}$$

$$K_b = \frac{[\text{BH}^+_{(aq)}][\text{OH}^-_{(aq)}]}{[\text{B}_{(aq)}]}$$

$K_b$ is called the dissociation constant for the weak base B.

There is an interesting relationship between the dissociation constant of an acid and that of its conjugate base.

<table>
<thead>
<tr>
<th>Acid</th>
<th>HA</th>
<th>Conjugate base</th>
<th>A^-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$K_a \times K_b = Kw$$

Therefore $K_a \times K_b = Kw$ for the dissociation of an acid and its conjugate base.
2. Uses of Ka and Kb (pKa and pKb) values to compare the strength of weak acids or weak bases

Note the difference between the concentration and strength of acids and bases. **Strength** refers to the degree of dissociation of an acid and a base; concentration refers to the number of moles of acid or base in a given volume of water. For example, 0.01 M hydrochloric acid is a dilute solution of a strong acid. 10 M ethanoic acid is a concentrated solution of a weak acid. 10 M NaOH\(_{\text{aq}}\) is a concentrated solution of a strong alkali.

Example 1

<table>
<thead>
<tr>
<th>Acid</th>
<th>0.10 M HCl(_{\text{aq}})</th>
<th>0.10 M CH(<em>3)COOH(</em>{\text{aq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ka / mol dm(^{-3})</td>
<td>1.0 x 10(^{7})</td>
<td>1.8 x 10(^{-5})</td>
</tr>
<tr>
<td>pH</td>
<td>1.0</td>
<td>2.9</td>
</tr>
<tr>
<td>([H_3O^+]_{\text{aq}}) / mol dm(^{-3})</td>
<td>0.10</td>
<td>1.3 x 10(^{-3})</td>
</tr>
<tr>
<td>([A^-]_{\text{aq}}) / mol dm(^{-3})</td>
<td>0.10</td>
<td>1.3 x 10(^{-3})</td>
</tr>
<tr>
<td>([HA]_{\text{aq}}) / mol dm(^{-3})</td>
<td>~ 0</td>
<td>~ 0.10</td>
</tr>
<tr>
<td>Degree of dissociation</td>
<td>~ 100%</td>
<td>~ 1.3%</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

The dissociation constant Ka for an acid indicates the extent of dissociation in a solution of an acid. Ka values can thus be used to compare the strength of weak acids.

Example 2

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ka / mol dm(^{-3})</th>
<th>pKa</th>
<th>Strength of acid</th>
<th>Conjugate base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1.0 x 10(^{7})</td>
<td>-7</td>
<td>Strong acid</td>
<td></td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>1.0 x 10(^{2})</td>
<td>-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSO(_4)(^-)</td>
<td>1.6 x 10(^{-2})</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)COOH</td>
<td>1.8 x 10(^{-5})</td>
<td>4.7</td>
<td>Weak acid</td>
<td></td>
</tr>
<tr>
<td>CH(_2)CH(_2)COOH</td>
<td>1.3 x 10(^{-5})</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)CO(_3)</td>
<td>4.3 x 10(^{-7})</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
<td>6.3 x 10(^{-10})</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO(_3)(^-)</td>
<td>4.8 x 10(^{-11})</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similarly, the dissociation constant Kb for a base indicates the extent of dissociation in a solution of a base. Kb values can also be used to compare the strength of weak base.

Example 3

<table>
<thead>
<tr>
<th>Base</th>
<th>Kb / mol dm(^{-3})</th>
<th>pKb</th>
<th>Strength of base</th>
<th>Conjugate acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_3)(^2-)</td>
<td>2.1 x 10(^{-4})</td>
<td>3.7</td>
<td>increasing</td>
<td></td>
</tr>
<tr>
<td>NH(_3)</td>
<td>1.7 x 10(^{-5})</td>
<td>4.8</td>
<td>base strength</td>
<td></td>
</tr>
<tr>
<td>HCO(_3)(^-)</td>
<td>2.3 x 10(^{-8})</td>
<td>7.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)COO(^-)</td>
<td>5.5 x 10(^{-10})</td>
<td>9.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Calculations involving pH, Ka and Kb

Example 1
(a) Calculate the pH of 0.50 mol dm$^{-3}$ NaOH$_{(aq)}$.

NaOH is a strong base, so assume [OH$^{-}(aq)$] = [NaOH$_{(aq)}$].

[OH$^{-}(aq)$] = 0.50 mol dm$^{-3}$

[H$_3$O$^+(aq)$][OH$^{-}(aq)$] = 1.00 x $10^{-14}$ mol$^2$ dm$^{-6}$

[H$_3$O$^+(aq)$] = 2.00 x $10^{-14}$ mol dm$^{-3}$

∴

pH = 13.7

(b) Calculate the pH of 1.0 x $10^{-8}$ mol dm$^{-3}$ HCl$_{(aq)}$.

As the solution under consideration is very dilute, the concentration of hydroxonium ions that results from the dissociation of water cannot be ignored.

Total $[H_3O^+(aq)] = [H_3O^+(aq)] + [H_3O^+(aq)]$

water HCl

Example 2

The Ka of methanoic acid is 1.78 x $10^{-4}$ mol dm$^{-3}$ at 298 K.

(a) Determine the pH and degree of dissociation of 1.00 mol dm$^{-3}$ HCOOH$_{(aq)}$.

(b) Determine the pH and degree of dissociation of 1.00 x $10^{-2}$ mol dm$^{-3}$ HCOOH$_{(aq)}$.

Example 3: Determination of Ka of a weak acid by pH measurement

Calculate Ka for a weak acid of pH 4.5 in a solution of concentration of 0.050 mol dm$^{-3}$. 

Example 4
Calculate the pH of a 0.10 mol dm$^{-3}$ solution of sodium ethanoate.
(At 298 K, $K_a = 1.8 \times 10^{-5}$ mol dm$^{-3}$ for CH$_3$COOH)

Example 5
Given that $K_b$ for ammonia is $1.74 \times 10^{-5}$ mol dm$^{-3}$ at 298 K.
(a) Calculate the pH of a 0.100 mol dm$^{-3}$ solution of ammonia.

(b) Calculate the pH of a 0.0500 mol dm$^{-3}$ solution of ammonium chloride.

Example 6: **Determination of $K_b$ of a weak base by pH measurement**
The pH of a 0.50 mol dm$^{-3}$ solution of ammonia at 298 K is 11.3. Calculate the $K_b$ value for ammonia at this temperature.
Example 7
Ethanedioic acid is a dibasic acid which dissociates in water by two stages.
(a) Write the equations and the expressions of dissociation constants for the first and second dissociation process.

(b) Ethanedioate ion acts as a base in water. Write the acid-base reaction involved and calculate the Kb value for the ethanedioate ion at 25 °C.
(At 25 °C, $K_1 = 6.5 \times 10^{-2}$ mol dm$^{-3}$ and $K_2 = 6.1 \times 10^{-5}$ mol dm$^{-3}$)

Example 8
(a) A solution of ethanoic acid has a pH of 2.86 at 298 K. In a titration, 23.8 cm$^3$ of this acid solution were neutralized by 25.0 cm$^3$ of 0.106 mol dm$^{-3}$ sodium hydroxide solution. Determine the Ka for ethanoic acid at 298 K.

(b) The degree of dissociation of ethanoic acid in 0.10 mol dm$^{-3}$ solution at a certain temperature is 0.014. Calculate the pH and pKa values at this temperature.

Example 9
The dissociation constant of $\text{H}_2\text{PO}_4^{-}(\text{aq})$ in water, Ka, is $6.2 \times 10^{-8}$ mol dm$^{-3}$ at 298 K.
(a) Calculate the pH at 298 K of an aqueous solution of 0.10 mol dm$^{-3}$ $\text{NaH}_2\text{PO}_4$.(aq).

(b) Calculate the pH at 298 K of an aqueous solution of 0.050 mol dm$^{-3}$ $\text{NaH}_2\text{PO}_4$.(aq) and 0.050 mol dm$^{-3}$ $\text{Na}_2\text{HPO}_4$.(aq).
1. Principles of buffer action

A buffer is a solution which resists the change in pH on addition of a small amount of acid, alkali or water. The pH of the buffer does not change on addition of a small amount of acid or alkali because the components in the buffer can convert the acid or alkali into weak acid or weak base, which is only slightly dissociated.

**Acidic buffer**

Acidic buffers contain high concentrations of an undissociated weak acid and its conjugate base. It is made by dissolving a weak acid and its sodium or potassium salt in water. The weak acid absorbs any additional \( \text{OH}^{-}(aq) \) and the conjugate base absorbs additional \( \text{H}^{+}(aq) \).

Example:

A solution of equal concentrations of ethanoic acid and sodium ethanoate constitutes an acidic buffer solution: its pH is below 7. In this buffer solution the equilibrium is:

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COO}^{-}(aq) + \text{H}_3\text{O}^{+}(aq) \quad (1)
\]

The addition of sodium ethanoate increases \([\text{CH}_3\text{COO}^{-}(aq)]\), which combines with \(\text{H}^{+}(aq)\) to restore \(K_a\). The solution then contains a high concentration of undissociated ethanoic acid and ethanoate ion, i.e. the weak acid and its conjugate base.

If a small amount of strong acid is added to the system, the hydroxonium ions added combine with \(\text{CH}_3\text{COO}^{-}(aq)\), giving \(\text{CH}_3\text{COOH}(aq)\).

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

This causes the position of the buffer equilibrium \((1)\) shift to the left. The pH change is therefore minimal as long as there is a high enough concentration of ethanoate ions present to react with the hydroxonium ions added.

If a small amount of strong alkali is added to the system, the hydroxide ions added react with ethanoic acid present in the buffer solution.

\[
\text{CH}_3\text{COOH}(aq) + \text{OH}^{-}(aq) \rightleftharpoons \text{CH}_3\text{COO}^{-}(aq) + \text{H}_2\text{O}(l)
\]

This causes the position of the buffer equilibrium \((1)\) shift to the right. The pH change is therefore minimal as long as there is a high enough concentration of ethanoic acid molecules present.

**The pH of an acidic buffer solution**

The pH of an acidic buffer solution can be calculated as follows:

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

From the above equation, the pH of the buffer depends only on the ratio of \([\text{A}^{-}(aq)]\) to \([\text{HA}(aq)]\), but not on their actual concentrations. When the buffer is diluted, the pH does not change because the ratio does not change. An effective buffering action is obtained at pH close to pKa.

When \([\text{A}^{-}(aq)] = [\text{HA}(aq)]\), the ratio = 1 and pH = pKa.
Basic buffer

Basic buffers contain high concentrations of an undissociated weak base and its conjugate acid. It is made by dissolving a weak base and one of its soluble salt in water. The weak base absorbs any additional H$_{\text{aq}}^+$ and the conjugate acid absorbs additional OH$_{\text{aq}}^-$.

Example:
A solution of equal concentrations of ammonia and ammonium chloride constitutes a basic buffer solution: its pH is above 7. In this buffer solution the equilibrium is:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad (\text{II})
\]

The addition of ammonium chloride increases [NH$_4^+$], which combines with OH$^-$ to restore K$_b$. The solution then contains a high concentration of undissociated ammonia and ammonium ion, i.e. the weak base and its conjugate acid.

If a small amount of strong acid is added to the system, the hydroxonium ions added combine with NH$_3$(aq), giving NH$_4^+$.

\[
\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(l)
\]

This causes the position of the buffer equilibrium (II) shift to the right. The pH change is therefore minimal as long as there is a high enough concentration of ammonia present to react with the hydroxonium ions added.

If a small amount of strong alkali is added to the system, the hydroxide ions added react with ammonium ions present in the buffer solution.

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

This causes the position of the buffer equilibrium (II) shift to the left. The pH change is therefore minimal as long as there is a high enough concentration of ammonium ions present.

The pH of a basic buffer solution

The pH of an acidic buffer solution can be calculated as follows:

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

Buffering capacity

If the concentration of the buffer system is high, the addition of small amounts of acid or alkali will not significantly affect the ratio [A$^-$] to [HA] or [BH$^+$] to [B$^-$]. The buffering capacity is better, i.e. the buffer is more resistant to pH change. A buffer solution also has a better buffering capacity if the ratio is close to 1.

Significance of buffers in industry and biological systems

Buffer solutions are used to calibrate indicators and pH meters, control pH of solutions in which chemical reactions are performed. In electroplating, an optimum pH is maintained by buffer in order to control the preferential discharge of ions and the plating quality. Buffer is also used in the preservation of food and medicines. Buffer is also important in biological systems, which are efficient within a narrow pH range. For example, the pH of blood is controlled within strict limits (7.4) for it contains various salts (e.g. hydrogencarbonate) which behave as buffers.
2. Calculations involving the composition and pH of buffer solutions

Example 1

The following solutions can act as a buffer:
(I) a solution with [CH$_3$COOH] = 0.100 mol dm$^{-3}$
    and [CH$_3$COO$^-$] = 0.075 mol dm$^{-3}$
(II) a solution with [CH$_3$COOH] = 1.000 mol dm$^{-3}$
    and [CH$_3$COO$^-$] = 0.750 mol dm$^{-3}$

(a) Calculate the approximate pH value of (I) and (II).
(Ka for ethanoic acid = 1.75 x 10$^{-5}$ mol dm$^{-3}$)

\[
pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]}
\]

(I) \[\text{pH} = - \log(1.75 \times 10^{-5}) + \log \frac{0.075}{0.100} = 4.63\]

(II) \[\text{pH} = - \log(1.75 \times 10^{-5}) + \log \frac{0.75}{1.000} = 4.63\]

(b) Which of the above solutions is the better buffer? Explain your answer.
Solution (II) is a better buffer. It has a higher concentration of both CH$_3$COOH and CH$_3$COO$^-$, and hence a large buffer capacity.

(c) Can a solution of ethanoic acid alone act as a buffer? Explain your answer.
No. Ethanoic acid is a weak acid. Its solution has a relatively small amount of CH$_3$COO$^-$. When a small amount of strong acid is added, the amount of CH$_3$COO$^-$ is not sufficient to react with the hydrogen ions produced by the strong acid.

Example 2

A solution of 0.100 mol dm$^{-3}$ methanoic acid and 0.400 mol dm$^{-3}$ sodium methanoate has a pH of 5.00. Calculate the acid dissociation constant of methanoic acid.

Example 3

What mass of sodium carbonate must be added to 0.50 dm$^3$ of 0.40 mol dm$^{-3}$ NaHCO$_3$(aq) solution in order to prepare a buffer solution at pH 9.5. Assume that the volume of the solution does not change when the solid is added.
(pKa for HCO$_3^-$ is 10.25 and molar mass of Na$_2$CO$_3$ is 106)
Example 4
If 2.50 g of ammonium chloride is added to 250 cm$^3$ of 0.100 mol dm$^{-3}$ ammonia solution at 298 K, what will the pH of the solution become?
(molar mass of ammonium chloride = 53.5 g mol$^{-1}$; Kb for ammonia at 298 K = $1.74 \times 10^{-5}$ mol dm$^{-3}$)

Example 5
What is the pH of a solution prepared by the addition of 50.0 cm$^3$ of 0.200 mol dm$^{-3}$ sodium hydroxide solution to 50.0 cm$^3$ of 0.400 mol dm$^{-3}$ ethanoic acid.
(Ka for ethanoic acid = $1.75 \times 10^{-5}$ mol dm$^{-3}$)

Example 6
What volume of 0.10 M KOH(aq) solution should be added to 100 cm$^3$ of 0.10 M ethanoic acid solution to give a buffer of pH = 5.20?
(Ka for ethanoic acid = $1.75 \times 10^{-5}$ mol dm$^{-3}$)
Example 7
1 dm$^3$ of a solution is obtained by mixing 500 cm$^3$ of 0.200 mol dm$^{-3}$ HCl and 500 cm$^3$ of 0.700 mol dm$^{-3}$ NaCN. Given that the dissociation constant of HCN is 4.00 x $10^{-10}$ mol dm$^{-3}$, calculate the pH of the solution.

Example 8
Given: Ka for CH$_3$(CH$_2$)$_2$COOH = 1.50 x $10^{-5}$ mol dm$^{-3}$ at 298 K. Calculate the pH of
(a) an aqueous solution of 0.050 mol dm$^{-3}$ CH$_3$(CH$_2$)$_2$COONa and 0.050 mol dm$^{-3}$ CH$_3$(CH$_2$)$_2$COOH;
(b) 1.0 dm$^3$ of the solution in (b) after the addition of 1.0 x $10^{-3}$ mol of solid NaOH. Compare this pH change to that which occurs when the same amount of NaOH solid is added to 1.0 dm$^3$ of water.

Example 9
A buffer solution is made by mixing equal volumes of 0.100 mol dm$^{-3}$ ethanoic acid and 0.200 mol dm$^{-3}$ sodium ethanoate. (Ka for ethanoic acid = 1.75 x $10^{-5}$ mol dm$^{-3}$)
(a) Determine the pH of the buffer.
(b) If 100 cm$^3$ of 0.100 mol dm$^{-3}$ NaOH is added to 1 dm$^3$ of the buffer, what will the pH of the buffer become?
(c) Calculate the pH of 1 dm$^3$ of the buffer after addition of 100 cm$^3$ of 0.100 mol dm$^{-3}$ HCl.
(5) **Indicators**

1. **Simple theory of acid-base indicators**

An ***acid-base*** indicator is a substance which change colour as the pH of the solution in which it is dissolved changes.

**Indicator as a weak acid, HIn**

An indicator is a weak acid whose conjugate base has a different colour from that of the acid.

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

The colour of solution depends on the relative concentrations of HIn and In⁻.

In acidic solution, \([\text{H}^+(aq)]\) increases. According to Le Chatelier’s principle, the position of the above equilibrium shifts to the left. \([\text{In}^{-}(aq)]\) decreases and the dissociation of HIn is suppressed. The colour of HIn (acidic colour) predominates.

In alkaline solution, the increased \(\text{OH}^{-}(aq)\) ions combine with \(\text{H}^+(aq)\) ions. According to Le Chatelier’s principle, equilibrium position shifts to the right to replace the \(\text{H}^+(aq)\). The intensity of the alkaline colour due to the anion In⁻ increases.

**Example 1**

Phenolphthalein (HPh), a weak acid with \(K_a = 5.0 \times 10^{-10} \text{ mol dm}^{-3}\), is a common acid-base indicator.

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

**Indicator as a weak base, In**

An indicator is a weak base whose conjugate acid has a different colour from that of the base.

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

The colour of solution depends on the relative concentrations of In and HIn⁺.

In acidic solution, \([\text{H}^+(aq)]\) increases. According to Le Chatelier’s principle, the position of the above equilibrium shifts to the right. \([\text{In}^{-}(aq)]\) decreases and the colour of HIn⁺ (acidic colour) predominates.

In alkaline solution, the increased \(\text{OH}^{-}(aq)\) ions react with HIn⁺(aq). According to Le Chatelier’s principle, equilibrium position shifts to the left. The intensity of the alkaline colour due to the In increases.

**Example 2**

The indicator methyl orange (M) is a weak base.

\[
\text{M}^{\text{aq}} + \text{H}_2\text{O}(l) \rightleftharpoons \text{MH}^+(aq) + \text{OH}^-(aq)
\]
2. **Colour changes and pH ranges of acid-base indicators**

Acid-base indicators are usually coloured organic compounds, the molecules of which can lose or gain protons. The change in molecular structure due to proton loss or gain results in a colour change, which depends on the **pH range** it is in. The list below shows the pH range of some common indicators during which a colour change can be seen.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>HIn</th>
<th>In$^-$</th>
<th>$K_{In}$/ mol dm$^{-3}$</th>
<th>$pK_{In}$</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>red</td>
<td>yellow</td>
<td>2.0 x 10$^{-4}$</td>
<td>3.7</td>
<td>3.1 – 4.4</td>
</tr>
<tr>
<td>Bromophenol blue</td>
<td>yellow</td>
<td>blue</td>
<td>1.0 x 10$^{-4}$</td>
<td>4.0</td>
<td>3.0 – 4.6</td>
</tr>
<tr>
<td>Methyl red</td>
<td>red</td>
<td>yellow</td>
<td>8.0 x 10$^{-6}$</td>
<td>5.1</td>
<td>4.2 – 6.3</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>yellow</td>
<td>blue</td>
<td>1.0 x 10$^{-7}$</td>
<td>7.0</td>
<td>6.0 – 7.6</td>
</tr>
<tr>
<td>Phenol red</td>
<td>yellow</td>
<td>red</td>
<td>1.0 x 10$^{-8}$</td>
<td>8.0</td>
<td>6.8 – 8.4</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>colourless</td>
<td>red</td>
<td>5.0 x 10$^{-10}$</td>
<td>9.3</td>
<td>8.3 – 10.0</td>
</tr>
</tbody>
</table>

There is not an abrupt colour change at one specific pH value. The shift in equilibrium produces a gradual decrease in one colour and increase in the other. The concentration of one coloured form of the indicator must usually be at least ten times that of the other for a change to be visible to the eyes.

$$
\text{acidic colour} \quad \text{HIn}^{\text{aq}} + \text{H}_2\text{O}^{\text{l}} \rightleftharpoons \text{In}^-^{\text{aq}} + \text{H}_3\text{O}^+^{\text{aq}} \\
\text{alkaline colour}
$$

The colour of the solution depends on the value of the ratio $[\text{In}^-^{\text{aq}}] / [\text{HIn}^{\text{aq}}]$. When this is very large, $[\text{In}^-^{\text{aq}}] > [\text{HIn}^{\text{aq}}]$, the colour is that of In$^-$; when this is small, $[\text{In}^-^{\text{aq}}] < [\text{HIn}^{\text{aq}}]$, the colour is that of HIn.

If $[\text{In}^-^{\text{aq}}] / [\text{HIn}^{\text{aq}}] = 10$ ,

If $[\text{In}^-^{\text{aq}}] / [\text{HIn}^{\text{aq}}] = 1/10$ ,

Therefore, most indicators change from one extreme of colour to the other over a range of about 2 pH units, i.e. pH range for an indicator to change colour is $pK_{In} \pm 1$.

Example

Phenolphthalein (HPh) is a common acid-base indicator with $K_a = 5.0 \times 10^{-10}$ mol dm$^{-3}$.

(a) Calculate the ratio of $[\text{Ph}^-] / [\text{HPh}]$ and predict the colour in a solution of pH = 8.0.

(b) Calculate the ratio of $[\text{Ph}^-] / [\text{HPh}]$ and predict the colour in a solution of pH = 9.3.

(c) Calculate the ratio of $[\text{Ph}^-] / [\text{HPh}]$ and predict the colour in a solution of pH = 10.5.
(6) Acid-base titrations

Titrations are methods of volumetric analysis. To determine the concentration of a given acid or base, standard solutions of acids or bases and a suitable indicator are required.

An indicator is used to detect the end-point in a titration. The end-point of a titration refers to the point at which the indicator for the titration has just changed colour. The equivalence point of titration refers to the point at which the reactants have just reacted with each other, according to the stoichiometric ratio given by the balanced equation of the reaction.

For an indicator to be useful, its end-point must be close to the equivalence point. At the equivalence point, the indicator should change over its whole range of colour on addition of one drop of the titrating solution. Otherwise, the equivalence point cannot be accurately detected by the indicator.

1. pH titration curve and the choice of indicators

Strong acid - strong base titration

In the titration of hydrochloric acid and sodium hydroxide solution, the concentration of hydrogen ions and the pH in the solution change with the volume of sodium hydroxide added.

<table>
<thead>
<tr>
<th>Volume of 0.1 M NaOH added to 25 cm³ of 0.1 M HCl</th>
<th>[H⁺(aq)] / mol dm⁻²</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.00</td>
<td>0.002</td>
<td>2.7</td>
</tr>
<tr>
<td>24.90</td>
<td>0.0002</td>
<td>3.7</td>
</tr>
<tr>
<td>24.95</td>
<td>0.0001</td>
<td>4.0</td>
</tr>
<tr>
<td>24.99</td>
<td>0.00002</td>
<td>4.7</td>
</tr>
<tr>
<td>25.00</td>
<td>0.0000001</td>
<td>7.0</td>
</tr>
<tr>
<td>25.05</td>
<td>10⁻¹⁰</td>
<td>10.0</td>
</tr>
</tbody>
</table>

The pH titration curve for strong acid-strong base reaction is shown below:

![pH titration curve](image)

In the strong acid-strong base titration curve, the pH change is very slight as the strong base is added. As the equivalence point is approach, the pH abruptly increases from 3 to 10. The curve is very steep. After the equivalence point, addition of base only changes the pH of the solution slightly. Since the change of pH near the equivalence point is so dramatic that there is a wide choice of suitable indicators. The end-point can be shown by any indicator which changes colour when the pH lies in the vertical part (pH 3 - 10) of the graph. Methyl orange, methyl red and phenolphthalein are all suitable indicators.
**Strong acid - weak base titration**

For a titration of a strong acid with a weak base, the pH at the equivalence point is always less than 7 because of the acidity of the conjugate acid of the weak base. After the equivalence point, the addition of more weak base increases the pH much more slowly because weak base does not dissociate readily to increase $[\text{OH}^-]$ greatly. Moreover, the buffering range of the system appears after the equivalence point. A suitable indicator should change colour within pH **3 – 7**, e.g. methyl orange and methyl red.

**Example 1**

Calculate the pH at the equivalent point when 25.0 cm$^3$ 0.100 mol dm$^{-3}$ HCl$(_{aq})$ is titrated with 0.100 mol dm$^{-3}$ NH$_3$$_{aq})$ . (K$_b$ for ammonia is $1.74 \times 10^{-5}$ mol dm$^{-3}$)

At the equivalence point, 25.0 cm$^3$ NH$_3$(aq) is added.

---

**Weak acid - strong base titration**

For a titration of a weak acid with a strong base, the buffering range of the system is established before the equivalence point. At the equivalence point, the pH is always greater than 7 because of the basicity of the conjugate base of the weak acid. After the equivalence point, the pH rises much faster because of the strong base added. An indicator must be chosen such that it changes colour within pH **7 – 11**, e.g. phenolphthalein.

**Example 2**

Calculate the pH at the equivalent point when 25.0 cm$^3$ 0.100 mol dm$^{-3}$ CH$_3$COOH$_{aq)}$ is titrated with 0.100 mol dm$^{-3}$ NaOH$_{aq)$ . (K$_a$ for ethanoic acid is $1.75 \times 10^{-5}$ mol dm$^{-3}$)

At the equivalence point, 25.0 cm$^3$ NaOH$_{aq)$ is added.
Weak acid – weak base titration

For a titration of a weak acid with a weak base, the change in pH at the end-point is gradual. Indicators will also change colour gradually. The pH curve does not rise steeply to give a marked colour change in any indicator, which indicates accurately the end-point. A pH meter or conductometric method is employed to detect the end-point.

Note that:

An **universal indicator** is prepared by mixing a number of indicators so that the mixture shows different colours from pH 1 – 14. Since the colour change is not sharp and clear-cut, it cannot be used to mark the end-point in titrations.

Example 3

50.0 cm$^3$ of a 0.100 mol dm$^{-3}$ solution of HCN(aq) was titrated with a strong base NaOH at 298 K. At the equivalence point of the titration, the pH was found to be 10.9. Calculate the volume of the base added to reach the equivalence point. Hence calculate the concentration of NaOH added. (Ka for HCN = 6.20 x 10$^{-10}$ mol dm$^{-3}$ at 298 K)
2. **Acid-base titrations using method of double indicator**

The titration curve for a dibasic acid or a tribasic acid has more than one inflection showing that there is more than one equivalence point.

The figure below shows the pH change during the titration of sodium carbonate with hydrochloric acid: 

\[
\text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{HCl}(\text{aq}) \rightleftharpoons 2 \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

There are two stages in the titration:

**Stage 1** \(\text{Na}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{aq}) + \text{NaHCO}_3(\text{aq})\)

Phenolphthalein changes from red to colourless at the end-point of this reaction, at pH = 8.5.

**Stage 2** \(\text{NaHCO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{aq}) + \text{CO}_2(g) + \text{H}_2\text{O}(l)\)

Methyl orange changes from yellow to orange at the end-point of this reaction, at pH = 4.0.

**Example**

A 25.0 cm\(^3\) portion of a solution containing sodium carbonate and sodium hydrogencarbonate needed 22.5 cm\(^3\) of a solution of hydrochloric acid of concentration 0.100 mol dm\(^{-3}\) to decolourize phenolphthalein. On addition of methyl orange, a further 28.5 cm\(^3\) of the acid were needed to turn this indicator to orange. Calculate the concentration of sodium carbonate and sodium hydrogencarbonate in the solution.
(7) Solubility product

1. Solubility product of a sparingly soluble electrolyte

When increasing quantities of a sparingly soluble electrolyte (ionic solid) are added to water, a saturated solution is eventually formed. Ions in the saturated solution are in equilibrium with the excess undissolved solute:

\[ \text{A}_x\text{B}_y(s) \rightleftharpoons x\text{A}^{y+}(aq) + y\text{B}^{x-}(aq) \]

Hence \[ K_c = \]

But, \([\text{A}_x\text{B}_y(s)]\), which represents the concentration of a pure solid, is constant.

So, \[ [\text{A}^{y+}(aq)]^x[\text{B}^{x-}(aq)]^y = \text{Ksp} \text{, the solubility product of A}_x\text{B}_y. \]

The solubility product of a sparingly soluble salt is essentially a modified equilibrium constant. Like other equilibrium constants, its value will change with temperature. Solubility normally increases with temperature, so this will result in an increase in the value of Ksp as temperature rises.

The solubility product concept is valid for saturated solutions in which the total concentration of ions is no more than about 0.01 M. For concentration greater than this, the value of Ksp is no longer constant. This means that it is quite inappropriate to use the solubility product concept for soluble compounds such as NaCl, CuSO₄ and AgNO₃.

Example

The table below shows the equilibrium concentrations of Ag⁺(aq) and BrO₃⁻(aq) in contact with undissolved AgBrO₃ when different initial volumes of 0.1 mol dm⁻³ AgNO₃ and 0.1 mol dm⁻³ KBrO₃ are added to 200 cm³ of distilled water at 16 °C.

<table>
<thead>
<tr>
<th>Initial volume of 0.1 M AgNO₃ / cm³</th>
<th>Initial volume of 0.1 M KBrO₃ / cm³</th>
<th>Concentration of Ag⁺(aq) at equilibrium / mol dm⁻³</th>
<th>Concentration of BrO₃⁻(aq) at equilibrium / mol dm⁻³</th>
<th>[Ag⁺(aq)][BrO₃⁻(aq)] / mol² dm⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10</td>
<td>0.0144</td>
<td>0.0024</td>
<td>3.45 x 10⁻⁵</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>0.0081</td>
<td>0.0041</td>
<td>3.32 x 10⁻⁵</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>0.0042</td>
<td>0.0082</td>
<td>3.44 x 10⁻⁵</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>0.0033</td>
<td>0.0102</td>
<td>3.37 x 10⁻⁵</td>
</tr>
</tbody>
</table>

The concentrations of BrO₃⁻ were obtained as follows. A measured volume of the aqueous solution was pipetted. Acid was then added followed by excess potassium iodide. The liberated iodine was then titrated against standard sodium thiosulphate solution. Once the concentration of BrO₃⁻(aq) was determined, the concentration of Ag⁺(aq) can be calculated.

Notice that the product of the concentrations of Ag⁺ and BrO₃⁻ is constant. It is independent of the amount of AgBrO₃ present, provided there is some undissolved AgBrO₃ in contact with the solution.

When equilibrium between pure AgBrO₃ and its ions is reached:

\[ \text{AgBrO}_3(s) \rightleftharpoons \text{Ag}^+(aq) + \text{BrO}_3^-(aq) \]

\[ [\text{Ag}^+(aq)][\text{BrO}_3^-(aq)] = \text{a constant at a given temperature} = 3.39 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \text{ at 16 °C} \]

This constant is known as the solubility product, Ksp, of AgBrO₃.
2. Calculation of Ksp from solubility and vice versa

The solubility product of a sparingly soluble salt is usually obtained from its solubility.

Example 1
A saturated solution of silver chloride contains 1.46 x 10^{-3} g dm^{-3} at 18 °C. What is the solubility product of silver chloride at this temperature? (Mr of AgCl = 143.5)

The solubility of silver chloride at 18 °C =

At equilibrium, \( \text{AgCl} (s) \rightleftharpoons \text{Ag}^{+} (aq) + \text{Cl}^{-} (aq) \)

\[
[\text{Ag}^{+} (aq)] = [\text{Cl}^{-} (aq)] = \quad \therefore \quad \text{Ksp} (\text{AgCl}) = [\text{Ag}^{+} (aq)] [\text{Cl}^{-} (aq)]
\]

Example 2
The solubility of calcium fluoride is 2.15 x 10^{-4} mol dm^{-3} at 25 °C. Calculate the solubility product of CaF_2 at this temperature.

Conversely, the solubility of a sparingly soluble salt can be obtained from its solubility product.

Example 3
The solubility product of silver carbonate at 20 °C is 8.00 x 10^{-12} mol^3 dm^{-9}. What is its solubility at this temperature?

At equilibrium, \( \text{Ag}_2\text{CO}_3 (s) \rightleftharpoons 2 \text{Ag}^{+} (aq) + \text{CO}_3^{2-} (aq) \)

If the solubility of Ag_2CO_3 is s mol dm^{-3},

\[
[\text{Ag}^{+} (aq)] = 2s \text{ mol dm}^{-3}
\]

\[
[\text{CO}_3^{2-} (aq)] = s \text{ mol dm}^{-3}
\]

\[
\text{Ksp} (\text{Ag}_2\text{CO}_3) = [\text{Ag}^{+} (aq)]^2 [\text{CO}_3^{2-} (aq)]
\]

The solubility of silver carbonate at 20 °C is

Example 4
The solubility product of lead(II) iodide at 25 °C is 7.10 x 10^{-9} mol^3 dm^{-9}. What is its solubility at this temperature?
3. Common ion effect

**Common ion effect:**
In the presence of either A⁺ or B⁻ from a second source, the solubility of the sparingly soluble salt AB is reduced.

Although the solubility product of a sparingly soluble salt is constant at constant temperature, the concentrations of the individual ions may vary over a very wide range. When a saturated solution is obtained by dissolving the pure salt in water the concentrations of the ions are in a ratio determined by the formula of the compound. For example, the concentrations of Ca²⁺ and F⁻ ions in pure saturated calcium fluoride solution must be in the ratio 1 : 2.

However, when a saturated solution is obtained by mixing two solutions containing a common ion, there may be a big different in the concentration of the ions of any sparingly soluble electrolyte.

Example 1
Consider the solubility of BaSO₄, first in water and then in 0.10 mol dm⁻³ sodium sulphate solution.

Given: \(K_{sp}(\text{BaSO}_4) = 1.00 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}\)

**Solubility of BaSO₄ in water:**
At equilibrium, \(\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})\)

If the solubility of BaSO₄ is \(s \text{ mol dm}^{-3}\),
\[
[\text{Ba}^{2+}(\text{aq})] = s \text{ mol dm}^{-3}
\]
\[
[\text{SO}_4^{2-}(\text{aq})] = s \text{ mol dm}^{-3}
\]

\(K_{sp}(\text{BaSO}_4) = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = \)

\[\therefore \text{ solubility of BaSO}_4 \text{ in water } = \]

**Solubility of BaSO₄ in 0.10 mol dm⁻³ Na₂SO₄(aq):**
Suppose the solubility of BaSO₄ in 0.10 mol dm⁻³ Na₂SO₄ = \(s' \text{ mol dm}^{-3}\).
At equilibrium, \(\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})\)

\[
[\text{Ba}^{2+}(\text{aq})] = s' \text{ mol dm}^{-3}
\]
\[
[\text{SO}_4^{2-}(\text{aq})] = (0.10 + s') \text{ mol dm}^{-3}
\]

\(K_{sp}(\text{BaSO}_4) = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = \)

\[\therefore \text{ solubility of BaSO}_4 \text{ in 0.10 mol dm}^{-3} \text{ Na}_2\text{SO}_4(\text{aq}) = \]

This calculation illustrates that BaSO₄ is less soluble in 0.10 mol dm⁻³ sodium sulphate solution than in pure water. As 0.10 mol dm⁻³ sodium sulphate solution contains SO₄²⁻ ions, they will add to the concentration of SO₄²⁻ and suppress the amount of BaSO₄ which can dissolve.

Example 2
Calculate the solubility of lead(II) chloride in (a) 0.10 M Pb(NO₃)₂(aq) solution and (b) 0.10 M NaCl(aq) solution at 298 K. \(K_{sp}(\text{PbCl}_2) = 2.0 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}\) at 298 K.
4. Predicting precipitation

Another important application of solubility products is that they enable chemists to predict the maximum concentrations of ions in a solution. Hence, it is possible to tell whether or not precipitation will occur.

Example 1
A 1.0 × 10⁻³ mol dm⁻³ solution of Ca²⁺ ions is mixed with an equal volume of 1.0 × 10⁻³ mol dm⁻³ solution of SO₄²⁻ ions at 25 °C. Will a precipitate of CaSO₄ form?

The solubility product for calcium sulphate is 2.0 × 10⁻⁵ mol² dm⁻⁶ at 25 °C.

Immediately after mixing equal volumes of the two solutions and before any precipitation has occurred,

\[
[Ca^{2+}\text{(aq)}] = [SO_4^{2-}\text{(aq)}] = \frac{(1.0 \times 10^{-3})}{2} = 5.0 \times 10^{-4} \text{ mol dm}^{-3}
\]

Hence, the ionic product for CaSO₄ immediately after mixing,

\[
[Ca^{2+}\text{(aq)}][SO_4^{2-}\text{(aq)}] = (5.0 \times 10^{-4})^2 = 2.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}
\]

This ionic product is less than the value of Ksp for CaSO₄, so no precipitate will form.

Suppose equal volumes of 1.0 × 10⁻² mol dm⁻³ solutions are mixed.

Immediately after mixing,

\[
[Ca^{2+}\text{(aq)}] = [SO_4^{2-}\text{(aq)}] = \frac{(1.0 \times 10^{-2})}{2} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}
\]

and the ionic product

\[
[Ca^{2+}\text{(aq)}][SO_4^{2-}\text{(aq)}] = (5.0 \times 10^{-3})^2 = 2.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}
\]

The ionic product is greater than the value of Ksp for CaSO₄. Therefore precipitation of CaSO₄ occurs. The concentration of aqueous Ca²⁺ and SO₄²⁻ ions are lowered by the reaction:

\[
Ca^{2+}\text{(aq)} + SO_4^{2-}\text{(aq)} \rightarrow CaSO_4(s)
\]

Example 2
When hydrogen sulphide is bubbled through a solution containing Cu²⁺, Zn²⁺ and Ni²⁺ ions, the following equilibrium is established:

\[
H_2S(\text{aq}) \rightleftharpoons 2 H^+\text{(aq)} + S^{2-}\text{(aq)}
\]

In acid solution, H⁺ ions will displace the equilibrium to the left. This reduces the concentrations of \(S^{2-}\text{(aq)}\) to very low values. Hence, only those metal sulphides with very low solubility products (such as CuS, Ksp (CuS) = 6.3 × 10⁻³⁶ mol² dm⁻⁶) will be precipitated. So, in acid solution:

\[
[Cu^{2+}\text{(aq)}][S^{2-}\text{(aq)}] > Ksp (CuS) = 6.3 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}
\]

\[
[Zn^{2+}\text{(aq)}][S^{2-}\text{(aq)}] < Ksp (ZnS) = 1.6 \times 10^{-24} \text{ mol}^2 \text{ dm}^{-6}
\]

\[
[Ni^{2+}\text{(aq)}][S^{2-}\text{(aq)}] < Ksp (NiS) = 4.0 \times 10^{-21} \text{ mol}^2 \text{ dm}^{-6}
\]

Thus CuS is precipitated, but ZnS and NiS do not precipitate.

In neutral solution, the concentration of \(S^{2-}\text{(aq)}\) from H₂S will be higher and this enables ZnS with a higher solubility product to precipitate as well as CuS.

When the solution is made slightly alkaline with ammonia, the H₂S equilibrium is displaced further to the right and the concentration of \(S^{2-}\text{(aq)}\) is even higher. Under these conditions, NiS is precipitated as well as CuS and ZnS.