12. Acid Base Equilibria

Bronsted-Lowry Definition of acid Base behaviour

| HCl (g) + H₂O (l) → H₃O⁺ (aq) + Cl⁻ (aq) |
| acid |
| base |
| acid |
| base |

Each acid is linked to a conjugate base on the other side of the equation.

HNO₃ + HNO₂ ⇌ NO₃⁻ + H₂NO₂⁺

Acid 1   Base 2   Base 1   Acid 2

HCOOH + CH₃(CH₂)₂COOH ⇌ HCOO⁻ + CH₃(CH₂)₂COOH₂⁺

Acid 1   Base 2   Base 1   Acid 2

In these reactions the substance with bigger Ka will act as the acid.

Calculating pH

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

Where [H⁺] is the concentration of hydrogen ions in the solution.

Calculating pH of strong acids

Strong acids completely dissociate

The concentration of hydrogen ions in a monoprotic strong acid will be the same as the concentration of the acid.

For HCl and HNO₃ the [H⁺(aq)] will be the same as the original concentration of the acid.

For 0.1M HCl the pH will be \(-\log[0.1] = 1.00\)

Always give pH values to 2d.p. In the exam

Finding [H⁺] from pH

\[ [H^+] = 1 \times 10^{-\text{pH}} \]

On most calculators this is done by pressing Inv (or 2ⁿᵈ function) → log → - number(pH)

Example 1

What is the concentration of HCl with a pH of 1.35?

\[ [H^+] = 1 \times 10^{-1.35} = 0.045M \]

Ionic Product for water

In all aqueous solutions and pure water the following equilibrium occurs: H₂O (l) ⇌ H⁺ (aq) + OH⁻ (aq)

This equilibrium has the following equilibrium expression

\[ K_c = \frac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]} \]

Rearrange to

\[ K_c \times [H_2O (l)] = [H^+(aq)] [OH^-(aq)] \]

Because [H₂O (l)] is much bigger than the concentrations of the ions, we assume its value is constant and make a new constant Kw

\[ Kw = [H^+(aq)] [OH^-(aq)] \]

Learn this expression

At 25°C the value of Kw for all aqueous solutions is \(1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}\)

The Kw expression can be used to calculate [H⁺(aq)] ions if we know the [OH⁻(aq)] ions and vice versa.

pKw

Sometimes Kw is quoted as pKw values

\[ p\text{Kw} = -\log Kw \text{ so } Kw = 10^{-p\text{Kw}} \]

If Kw = \(1 \times 10^{-14}\) then pKw = 14
Finding pH of pure water

Pure water/ neutral solutions are neutral because the \([H^+_{(aq)}] = [OH^-_{(aq)}]\)

Using \(K_w = [H^+_{(aq)}][OH^-_{(aq)}]\) then when neutral \(K_w = [H^+_{(aq)}]^2\)
and \([H^+_{(aq)}] = \sqrt{K_w}\)
At 25°C \([H^+_{(aq)}] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}\) so pH = 7

At different temperatures to 25°C the pH of pure water changes. Le Chatelier’s principle can predict the change. The dissociation of water is endothermic so increasing the temperature would push the equilibrium to the right giving a bigger concentration of \(H^+\) ions and a lower pH.

Calculating pH of Strong Base

For bases we are normally given the concentration of the hydroxide ion.
To work out the pH we need to work out \([H^+_{(aq)}]\) using the \(K_w\) expression.

Strong bases completely dissociate into their ions. \(NaOH \rightarrow Na^+ + OH^-\)

Example 3: What is the pH of the strong base 0.1M \(NaOH\)
Assume complete dissociation.
\(K_w = [H^+_{(aq)}][OH^-_{(aq)}] = 1 \times 10^{-14}\)
\([H^+_{(aq)}] = Kw / [OH^-_{(aq)}] = 1 \times 10^{-14} / 0.1 = 1 \times 10^{-13}\) M
\(pH = - \log{1 \times 10^{-13}} = 13.00\)

Weak acids

Weak acids only slightly dissociate when dissolved in water, giving an equilibrium mixture

\(HA + H_2O (l) \rightleftharpoons H_2O^+_{(aq)} + A^-_{(aq)}\)

We can simplify this to

\(HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}\)

Weak acids dissociation expression

\(K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}\)

The \(K_a\) for ethanoic acid is \(1.7 \times 10^{-5}\) mol dm\(^{-3}\).

The larger \(K_a\) the stronger the acid

Calculating pH of a weak acid

To make the calculation easier two assumptions are made to simplify the \(K_a\) expression:
1) \([H^+_{(aq)}]_{eqm} = [A^-_{(aq)}]_{eqm}\) because they have dissociated according to a 1:1 ratio.
2) As the amount of dissociation is small we assume that the initial concentration of the undissociated acid has remained constant.

So \([HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}\)

\(K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}\)
Simplifies to
\(K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]_{initial}}\)
Example 5 What is the pH of a solution of 0.01M ethanoic acid (\(k_a\) is 1.7 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\))?

\[
\text{CH}_3\text{CO}_2\text{H}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{CH}_3\text{CO}_2^-_{(aq)}
\]

\[
\frac{[\text{H}^+_{(aq)}][\text{CH}_3\text{CO}_2^-_{(aq)}]}{[\text{CH}_3\text{CO}_2\text{H}_{(aq)}]} = \frac{1.7 \times 10^{-5}}{0.01} = 1.7 \times 10^{-4}
\]

\[
[\text{H}^+_{(aq)}]^2 = 1.7 \times 10^{-5} \times 0.01 = 1.7 \times 10^{-6}
\]

\[
[\text{H}^+_{(aq)}] = \sqrt{1.7 \times 10^{-6}} = 4.12 \times 10^{-4}
\]

\[
\text{pH} = -\log[\text{H}^+] = -\log(4.12 \times 10^{-4}) = 3.38
\]

Example 6 What is the concentration of propanoic acid with a pH of 3.52 (\(k_a\) is 1.35 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\))?

\[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{CH}_3\text{CH}_2\text{CO}_2^-_{(aq)}
\]

\[
[\text{H}^+_{(aq)}] = 1 \times 10^{-3.52} = 0.000302 \text{M}
\]

\[
\frac{[\text{H}^+_{(aq)}][\text{CH}_3\text{CH}_2\text{CO}_2^-_{(aq)}]}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(aq)}]} = \frac{1.35 \times 10^{-5}}{0.000302} = 4.49 \times 10^{-3}
\]

\[
[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(aq)}] = 9.12 \times 10^{-3} / 1.35 \times 10^{-5} = 6.75 \times 10^{-3} \text{ M}
\]

Working out pH of a weak acid at half equivalence

When a weak acid has been reacted with exactly half the neutralisation volume of alkali, the above calculation can be simplified considerably.

\[
\text{ka} = [\text{H}^+][\text{CH}_3\text{CO}_2^-] / [\text{CH}_3\text{CO}_2\text{H}] \quad \text{At half neutralisation we can make the assumption that [HA] = [A-]}
\]

So \([\text{H}^+_{(aq)}] = \text{ka}\)

And pH = pka

Example 7 What is the pH of the resulting solution when 25 cm\(^3\) of 0.1M NaOH is added to 50 cm\(^3\) of 0.1M CH\(_3\)COOH (\(k_a\) 1.7 \(\times\) 10\(^{-5}\) )

From the volumes and concentrations spot it is half neutralisation (or calculate)

\[
\text{pH} = \text{pka} = -\log(1.7 \times 10^{-5}) = 4.77
\]

Diluting an acid or alkali

<table>
<thead>
<tr>
<th>pH of diluted strong acid</th>
<th>pH of diluted base</th>
</tr>
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</table>
| \([\text{H}^+_{(aq)}] = [\text{H}^+]_{\text{old}} \times \text{old volume}
\text{new volume} \)
| \([\text{H}^+] = K_w / [\text{OH}^-] \)
| pH = -\log[H^+]

Example 8 Calculate the new pH when 50.0 cm\(^3\) of 0.150 mol dm\(^{-3}\) HCl is mixed with 500 cm\(^3\) of water.

\[
[\text{H}^+] = [\text{H}^+]_{\text{old}} \times \text{old volume}
\text{new volume} \]

\[
[\text{H}^+_{(aq)}] = 0.150 \times \frac{0.05}{0.55} = 0.0136
\]

\[
\text{pH} = -\log[\text{H}^+] = -\log 0.0136 = 1.87
\]

Comparing the pH of a strong acid and a weak acid after dilution 10, 100 and 1000 times

Because pH is a logarithmic scale, diluting a strong acid 10 times will increase its pH by one unit, and diluting it 100 times would increase its pH by two units.

Weak acids would not change in the same way as when they are diluted. They increase by less than 1 unit.

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

Diluting the weak acid pushes the equilibrium to the right so the degree of dissociation increases and more \(\text{H}^+\) ions are produced meaning pH increases less than expected.
Buffer Solutions

A Buffer solution is one where the pH does not change significantly if small amounts of acid or alkali are added to it.

An acidic buffer solution is made from a weak acid and a salt of that weak acid (made from reacting the weak acid with a strong base).

Example: ethanoic acid and sodium ethanoate
\[ \text{CH}_3\text{CO}_2\text{H}^{(aq)} \text{ and CH}_3\text{CO}_2^- \text{Na}^+ \]

A basic buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid).

Example: ammonia and ammonium chloride \( \text{NH}_3 \) and \( \text{NH}_4^-\text{Cl}^- \)

How Buffer solutions work

In an ethanoic acid buffer

\[
\text{CH}_3\text{CO}_2\text{H}^{(aq)} \rightleftharpoons \text{CH}_3\text{CO}_2^-^{(aq)} + \text{H}^+^{(aq)}
\]

Acid          conjugate base

In a buffer solution there is a much higher concentration of the salt \( \text{CH}_3\text{CO}_2^- \) ion than in the pure acid.

The buffer contains a reservoir of HA and A⁻ ions

If small amounts of acid is added to the buffer: Then the above equilibrium will shift to the left removing nearly all the \( \text{H}^+ \) ions added, \( \text{CH}_3\text{CO}_2^- \text{(aq)} + \text{H}^+ \text{(aq)} \rightarrow \text{CH}_3\text{CO}_2\text{H}^{(aq)} \).

As there is a large concentration of the salt ion in the buffer the ratio \( [\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^-] \) stays almost constant, so the pH stays fairly constant.

If small amounts of alkali is added to the buffer. The OH⁻ ions will react with \( \text{H}^+ \) ions to form water.

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

The Equilibrium will then shift to the right to produce more \( \text{H}^+ \) ions.

\[ \text{CH}_3\text{CO}_2\text{H}^{(aq)} \rightleftharpoons \text{CH}_3\text{CO}_2^-^{(aq)} + \text{H}^+^{(aq)} \]

Some ethanoic acid molecules are changed to ethanoate ions but as there is a large concentration of the salt ion in the buffer the ratio \( [\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^-] \) stays almost constant, so the pH stays fairly constant.

Calculating the pH of buffer solutions

We still use the weak acids dissociation expression

\[ \text{Ka} = \frac{[\text{H}^+^{(aq)}][\text{A}^-^{(aq)}]}{[\text{HA}^{(aq)}]} \]

But here we assume the \( [\text{A}^-] \) concentration is due to the added salt only

Normally we rearrange to

\[ [\text{H}^+^{(aq)}] = \text{Ka} \frac{[\text{HA}^{(aq)}]}{[\text{A}^-^{(aq)}]} \]

We also assume the Initial concentration of the acid has remained constant, because amount that has dissociated or reacted is small.
Example 9: making a buffer by adding a salt solution

What would be the pH of a buffer made from 45 cm$^3$ of 0.1M ethanoic acid and 50 cm$^3$ of 0.15 M sodium ethanoate (Ka = 1.7 x 10$^{-5}$)?

Work out the moles of both solutions
Moles ethanoic = conc x vol = 0.1 x 0.045 = 0.0045 mol
Moles sodium ethanoate = conc x vol = 0.15 x 0.050 = 0.0075 mol

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

\[ [\text{H}^+] = 1.7 \times 10^{-5} \times \frac{0.0045}{0.0075} \implies [\text{H}^+] = 1.02 \times 10^{-5} \]

pH = -$\log [\text{H}^+]$
\[
= -\log 1.02 \times 10^{-5}
= 4.99
\]

Example 10: making a buffer by adding a solid salt

A buffer solution is made by adding 1.1 g of sodium ethanoate into 100 cm$^3$ of 0.4M ethanoic acid. What is its pH? Ka = 1.7 x 10$^{-5}$

Moles ethanoic = conc x vol = 0.4 x 0.1 = 0.04 mol
Moles sodium ethanoate = mass/Mr = 1.1/82 = 0.0134 mol

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

\[ [\text{H}^+] = 1.7 \times 10^{-5} \times \frac{0.04}{0.0134} \implies [\text{H}^+] = 5.07 \times 10^{-5} \]

pH = -$\log [\text{H}^+]$
\[
= -\log 5.07 \times 10^{-5}
= 4.29
\]

If a buffer is made by adding sodium hydroxide to partially neutralise a weak acid then follow the method below

Example 11: 55 cm$^3$ of 0.5 M CH$_3$CO$_2$H is reacted with 25 cm$^3$ of 0.35 M NaOH. What will be the pH of the resulting buffer solution?

Moles CH$_3$CO$_2$H = conc x vol = 0.5 x 0.055 = 0.0275 mol
Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875 mol
Moles of CH$_3$CO$_2$H in excess = 0.0275 - 0.00875 = 0.01875 (as 1:1 ratio)

[CH$_3$CO$_2$H] = moles excess CH$_3$CO$_2$H / total volume (dm$^3$)
= 0.01875/ 0.08 = 0.234 M

[CH$_3$CO$_2$$^-$] = moles OH$^-$ added / total volume (dm$^3$)
= 0.00875/ 0.08 = 0.109 M

\[ \text{ka} = \frac{[\text{H}^+] [\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} \]
\[ [\text{H}^+] = \text{ka} x \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]} \]
\[ = 1.7 \times 10^{-5} \times 0.234 / 0.109 \]
\[ = 3.64 \times 10^{-5} \]

pH = -$\log [\text{H}^+]$
\[
= -\log 3.64 \times 10^{-5}
= 4.44
\]

Buffering action in blood

A carbonic acid–hydrogencarbonate equilibrium acts as a buffer in the control of blood pH.

The H$_2$CO$_3$/HCO$_3^-$ buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

Equilibrium

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

Adding alkali reacts with H$^+$ so the above Equilibrium would shift right forming new H$^+$ and more HCO$_3^-$.
Calculating change in pH of buffer on addition of small amount of acid or alkali

If a small amount of alkali is added to a buffer then the moles of the buffer acid would reduce by the number of moles of alkali added and the moles of salt would increase by the same amount so a new calculation of pH can be done with the new values

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

If a small amount of acid is added to a buffer then the moles of the buffer salt would reduce by the number of moles of acid added and the moles of buffer acid would increase by the same amount so a new calculation of pH can be done with the new values

\[
\text{CH}_3\text{CO}_2\text{O}^{-}^{\text{(aq)}} + \text{H}^{\text{+}} \rightarrow \text{CH}_3\text{CO}_2\text{H}^{\text{(aq)}}
\]

**Example 12:** 0.005 mol of NaOH is added to 500cm³ of a buffer where the concentration of ethanoic acid is 0.200 mol dm⁻³ and the concentration of sodium ethanoate is 0.250 mol dm⁻³. (\(\text{Ka} = 1.7 \times 10^{-5}\))

Calculate the pH of the buffer solution after the NaOH has been added.

**Work out the moles of acid and salt in the initial buffer solution**
Moles ethanoic acid = conc x vol = 0.200 x 0.500 = 0.100mol
Moles sodium ethanoate = conc x vol = 0.25 x 0.500 = 0.125mol

**Work out the moles of acid and salt in buffer after the addition of 0.005mol NaOH**
Moles ethanoic acid = 0.100 - 0.005 = 0.095 mol
Moles sodium ethanoate = 0.125 + 0.005 = 0.130 mol

\[
\left[\text{H}^{\text{+}}\right] = \text{Ka} \times \frac{[\text{CH}_3\text{COOH}^{\text{(aq)}}]}{[\text{CH}_3\text{COO}^{-}^{\text{(aq)}}]}
\]

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

\[
\left[\text{H}^{\text{+}}\right] = 1.7 \times 10^{-5} \times \frac{0.095}{0.130} \Rightarrow \left[\text{H}^{\text{+}}\right] = 1.24 \times 10^{-5} \quad \text{pH} = -\log \left[\text{H}^{\text{+}}\right] = -\log 1.24 \times 10^{-5} = 4.91
\]
Titration curves

**Constructing a PH curve**

- Measure initial pH of the acid
- Add alkali in small amounts noting the volume added
- Stir mixture to equalise the pH
- Measure and record the pH to 1 dp
- When approaching endpoint add in smaller volumes of alkali
- Add until alkali in excess

Calibrate meter first by measuring known pH of a buffer solution. This is necessary because pH meters can lose accuracy on storage.

Can improve accuracy by maintaining constant temperature.

There are 4 main types of curve
1. Strong acid and strong base
2. Weak acid and strong base
3. Strong acid and weak base
4. Weak acid and weak base

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**Strong acid – Strong base** e.g. HCl and NaOH

At the start the pH rises quickly and then levels off. The flattened part is called the buffer region and is formed because a buffer solution is made.

Measuring the volume at neutralisation is important for most titrations.

You may also have to work out the neutralisation volume from titration data given in the question. These are done by standard titration calculations from module 1.

The equivalence point lies at the mid point of the extrapolated vertical portion of the curve.

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**Weak acid – Strong base** e.g. CH$_3$CO$_2$H and NaOH

For weak acids

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

At $\frac{1}{2}$ the neutralisation volume the $[HA] = [A^-]$

So $K_a = [H^+]$ and $pK_a = pH$

If we know the $K_a$ we can then work out the pH at $\frac{1}{2}$ V or vice versa.

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The Key points to sketching a curve:
- Initial and final pH
- Volume at neutralisation
- General Shape (pH at neutralisation)
**Choosing an Indicator**

Indicators can be considered as weak acids. The acid must have a different colour to its conjugate base.

An indicator changes colour from $\text{HIn}$ to $\text{In}^-$ over a narrow range. Different indicators change colours over different ranges.

The end-point of a titration is reached when $[\text{HIn}] = [\text{In}^-]$. To choose a correct indicator for a titration one should pick an indicator whose end-point coincides with the equivalence point for the titration.

An indicator will work if the pH range of the indicator lies on the vertical part of the titration curve. In this case the indicator will change colour rapidly and the colour change will correspond to the neutralisation point.

**Enthalpy change of Neutralisation**

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.

Enthalpy changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the values are similar, with values between -56 and -58 kJ mol\(^{-1}\) because the same reaction is occurring $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

Weak acids have a less exothermic enthalpy change of neutralisation because energy is absorbed to ionise the acid and break the bond to the hydrogen in the un-dissociated acid.