
1.12 Acids, bases and buffers

Acid reactions – a recap:

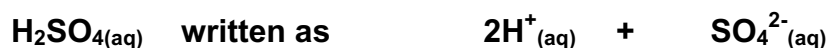
- a) Metal + Acid → Salt + Hydrogen
- b) Metal Oxide + Acid → Salt + Water
- c) Metal Hydroxide + Acid → Salt + Water
- d) Metal Carbonate + Acid → Salt + Water + Carbon dioxide
- e) Ammonia + Acid → Ammonium salt

Ionic equations

1. Ionic compounds when dissolved in water separate out into their constituent ions
2. This allows us to look at the actual aqueous ions involved in the reaction.
3. Ions that are not involved in reactions are called **spectator ions** as they do little more than 'watch' the reaction.

Rules:

1. All acids are (aq) therefore can be written with their acidic hydrogens dissociated:



2. All soluble ionic compounds, (aq) ions dissociated:



3. All insoluble ionic compounds, (s) ions will NOT dissociate:

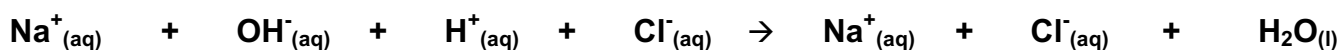


Example 1:

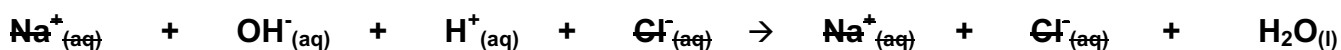
1. Write the full balanced chemical equation



2. Separate any ionic or acids species found with an aqueous state symbols



3. Identify and cross out the spectator ions



1. Rewrite the **balanced ionic equation** without the spectator ions



Bronsted - Lowrey acids and bases:

Definitions:

Acid:

Proton donor – releases H^+ ions when mixed with water

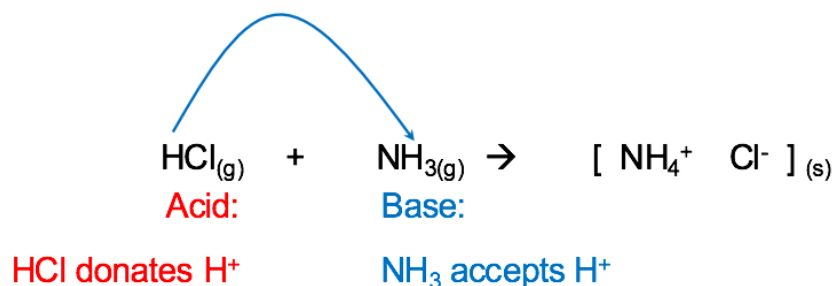
Base:

Proton acceptor – accepts H^+ ions when mixed with water

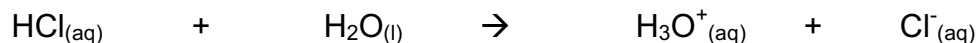
Alkali:

A base that dissolves in water releasing OH^- ions

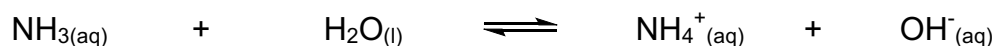
Transfer of protons:



Water as an acid and a base:



1. HCl donates a proton to water – acid
2. **H₂O** accepts a proton from HCl – **base**

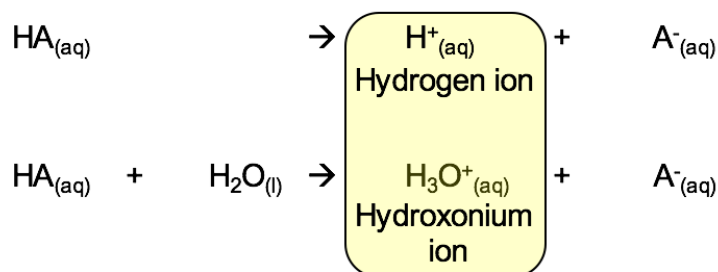


3. NH₃ accepts a proton from water – base
4. **H₂O** donates a proton to NH₃ – **acid**

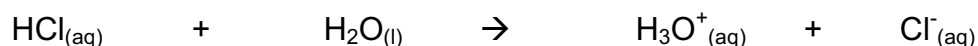
Protons in solution

- **Hydrogen ion, H⁺** and **proton** are the same.
- In water acids dissociate:

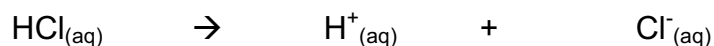
Acid dissociation, HA:



- In reality H⁺ ions are not on their own.
- They combine with water making the **hydroxonium ion**
- The hydrogen ion in the first reaction is actually the hydroxonium ion but we tend to leave it as the first reaction as it allows us to see how the acid behaves.
- H⁺_(aq) is the same as H₃O⁺_(aq)



Usually written as:

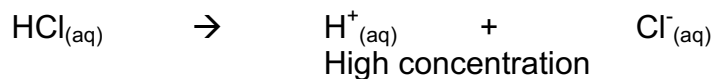


Strong and weak acids:

Definitions:

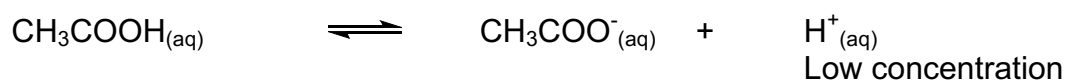
Strong acid:

Fully dissociate in water

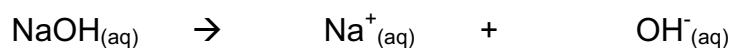


Weak acid:

Partially dissociate in water

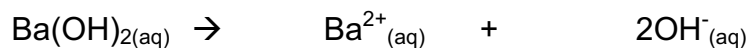


Dissociation of bases / alkalis:



- Sodium hydroxide completely ionises in water.

Other examples:

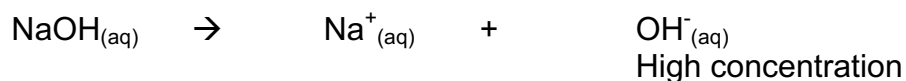


Strong and weak bases / alkali:

Definitions:

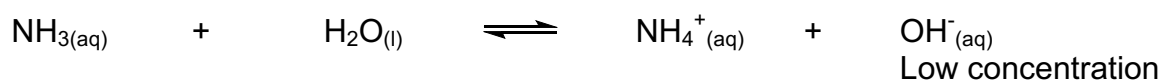
Strong base:

Fully dissociate in water

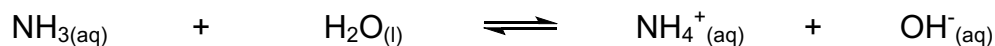


Weak base:

Partially dissociate in water



Acid – base equilibria:



Forward reaction:

- NH_3 accepts a proton from H_2O – base
- H_2O donates a proton to NH_3 – acid

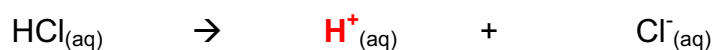
Reverse reaction reaction:

- NH_4^+ donates a proton to H_2O – acid
- OH^- accepts a proton from NH_4^+ – base

Mono, di and tri - basic acids:

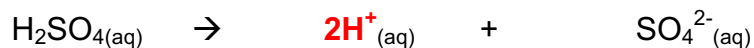
- Acids are categorised on the number of acidic hydrogen's / protons they can release:

Monobasic: releases 1 proton



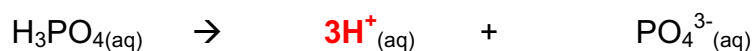
- $[\text{HCl}] = 1 \text{ mol dm}^{-3}$ $[\text{H}^+] = 1 \text{ mol dm}^{-3}$

Dibasic: releases 2 protons



- $[\text{H}_2\text{SO}_4] = 1 \text{ mol dm}^{-3}$ $[\text{H}^+] = 2 \text{ mol dm}^{-3}$

Tribasic: releases 3 protons



- $[\text{H}_3\text{PO}_4] = 1 \text{ mol dm}^{-3}$ $[\text{H}^+] = 3 \text{ mol dm}^{-3}$

The ionic product of water, K_w

- Water plays a big part in the understanding of acids.
- In order to understand acids then we need to understand water first:

Water: facts and models

Water conducts electricity. It has a conductivity of $26.6 \times 10^{-6} \text{ Scm}^{-1}$

- The fact that water conducts at all means that there must be at least some ions present:



- This means that water would have an equilibrium expression:

$$K_c = \frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- Rearrange this to:

$$K_c \times [\text{H}_2\text{O}] = [\text{H}^+] \times [\text{OH}^-]$$

- $[\text{H}_2\text{O}]$ of water in water is **constant** as the amount of dissociation is minimal.
- K_c is also a **constant**.
- These 2 terms can be replaced with one constant which we call:
- K_w , the **ionic product of water**

$$K_c \times [\text{H}_2\text{O}] = [\text{H}^+] \times [\text{OH}^-]$$

$$K_w = [\text{H}^+] \times [\text{OH}^-]$$

K_w has an equilibrium constant of 1×10^{-14}

ionic product of water:

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

PH and the ionic product of water

$$K_w = [H^+] \times [OH^-]$$

- Where K_w is known as the **ionic product of water**.
- At 298K the ionic product of water is $1 \times 10^{-14} \text{ Mol}^2 \text{ dm}^{-6}$.

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

- The protons and hydroxides are both produced from the dissociation of water.



- This means that the concentrations of both of these ions must be the same (as they both came from water).

$$[H^+] = [OH^-]$$

- This means that in pure water at equilibrium:

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

$$[H^+]^2 = 1 \times 10^{-14}$$

$$[H^+] = \sqrt{1 \times 10^{-14}}$$

$$[H^+] = 1 \times 10^{-7}$$

- The concentration of both ions produced by the dissociation of water = $1 \times 10^{-7} \text{ Mol dm}^{-3}$
- The the **pH of water = 7**
- A **negative logarithmic scale** compresses the values into a smaller range and flips the values, more useful to use as comparisons.
- This is the origin of the pH scale which gives us a relationship between pH and the hydrogen concentration:

pH

$$pH = -\log_{10} [H^+_{(aq)}]$$

$$pH = -\log_{10} [1 \times 10^{-7}]$$

$$pH = 7$$

The significance of K_w :

- K_w is basically an equilibrium expression linking $[H^+]$ and $[OH^-]$.
- We have already seen that at the **pH of water = 7** when the $[H^+] = [OH^-]$.

$$K_w = [H^+] \times [OH^-]$$

Acidic conditions $[H^+] > [OH^-]$.
Alkaline conditions $[H^+] < [OH^-]$.

The link between $[H^+]$, $[OH^-]$ and pH

- The $[H^+]$ and $[OH^-]$ are linked by the ionic product of water.

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

pH	1	3	5	7	9	11	13
$[H^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[OH^-]$	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}
$[H^+] \times [OH^-]$	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}	10^{-14}

- pH is linked to $[H^+]$
- This means $[H^+]$, $[OH^-]$ and pH are all linked:

The pH scale

OR

$$pH = -\log_{10} [H^+_{(aq)}]$$
$$[H^+_{(aq)}] = 10^{-pH}$$

What does pH mean:

Low pH **High $[H^+_{(aq)}]$**
High pH **Low $[H^+_{(aq)}]$**

Temperature. K_w and pH:

- The dissociation of water is an endothermic process:



- As temperature increases the equilibrium would move to the endothermic side.
- This means that more water would dissociate.
- Which means that K_w would increase as temperatures increase.
- Which means that the pH (neutral) would decrease:

Temperature / K	273	298	323
K_w	0.114×10^{-14}	1.008×10^{-14}	5.476×10^{-14}
pH (neutral)	7.47	7.00	6.63

- Calculations are therefore assumed to be at 298K (25°C)
- You must however appreciate that a different value for K_w could be used if at different temperatures (ie in biological systems)

Converting between pH and $[\text{H}^+_{(aq)}]$

- $[\text{H}^+_{(aq)}]$ and pH are not usually whole numbers and may not be in standard form.
- To calculate the pH or $[\text{H}^+]$ you will need a calculator.
- You will be expected to calculate the pH of:
 - 1) Strong acids
 - 2) Strong bases
 - 3) Weak acids
 - 4) Buffer solutions

1) a) Calculating the pH of strong acids:

- Strong acids – donate protons to water completely



- This means that for **strong acids** the $[\text{H}^+_{(aq)}] = [\text{ACID}]$

Examples:

1) Calculate the pH of $1 \times 10^{-3} \text{ mol dm}^{-3}$ HCl:

$$[\text{HCl}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$$\text{pH} = -\log [1 \times 10^{-3}]$$

$$\text{pH} = 3.0$$

2) Calculate the pH of $1 \times 10^{-6} \text{ mol dm}^{-3}$ HNO₃

$$[\text{HNO}_3] = 1 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 1 \times 10^{-6} \text{ mol dm}^{-3}$$

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

$$\text{pH} = -\log [1 \times 10^{-6}]$$

$$\text{pH} = 6.0$$

3) Calculate the pH of $1 \times 10^{-3} \text{ mol dm}^{-3}$ H₂SO₄

$$[\text{H}_2\text{SO}_4] = 1 \times 10^{-3} \text{ mol dm}^{-3} \quad * \text{ A dibasic acid so } \times 2 \text{ for } [\text{H}^+]$$

$$[\text{H}^+] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log [\text{H}^+_{(aq)}]$$

$$\text{pH} = -\log [2 \times 10^{-3}]$$

$$\text{pH} = 2.7$$

b) Calculating the $[H^+]$ of strong acids:

Examples:

1) Calculate the hydrogen ion concentration of an acid with a pH = 3

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-3}$$

$$[H^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

2) Calculate the hydrogen ion concentration of an acid with a pH = 2.4

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-2.4}$$

$$[H^+] = 3.98 \times 10^{-3} \text{ mol dm}^{-3}$$

3) Calculate the hydrochloric acid concentration with a pH = 2

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-2}$$

$$[H^+] = 0.01 \text{ mol dm}^{-3} \quad * \text{ HCl is a monobasic acid: } [H^+] = [HCl]$$

$$[HCl] = 0.01 \text{ mol dm}^{-3}$$

4) Calculate the sulphuric acid concentration with a pH = 2.6

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-2.6}$$

$$[H^+] = 2.5 \times 10^{-3} \text{ mol dm}^{-3} \quad * \text{ H}_2\text{SO}_4 \text{ is a dibasic acid: } 2 \times [H^+] \text{ per } [H_2SO_4]$$

$$[H_2SO_4] = 2.51 \times 10^{-3} / 2 \quad * \text{ Therefore divide by 2}$$

$$[H_2SO_4] = 1.26 \times 10^{-3} \text{ mol dm}^{-3}$$

Questions:

1) Calculate the pH of the following strong acids:

a) 0.1 Mol dm⁻³ HCl

b) 0.01 Mol dm⁻³ HNO₃

c) 0.001 Mol dm⁻³ HBr

d) 0.05 Mol dm⁻³ H₂SO₄

e) 0.1 Mol dm⁻³ H₃PO₄

f) 0.005 Mol dm⁻³ H₂SO₄

2) Calculate the [H⁺] of the following strong acids:

a) HCl with a pH = 2

b) HNO₃ with a pH = 3

c) HBr with a pH = 4

d) H₂SO₄ with a pH = 2

e) H₃PO₄ with a pH = 1.3

f) H₂SO₄ with a pH = 0

3) Calculate the concentration of each of the strong acids above:

a) HCl with a pH = 2

b) HNO₃ with a pH = 3

c) HBr with a pH = 4

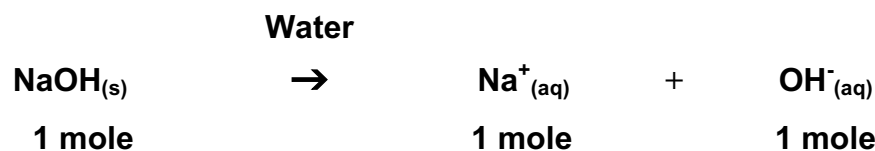
d) H₂SO₄ with a pH = 2

e) H₃PO₄ with a pH = 1.3

f) H₂SO₄ with a pH = 0

2) pH of strong bases

- Strong bases – dissociate completely to generate OH⁻ ions in water



- We use the **ionic product of water** to calculate the corresponding [H⁺] concentration for bases:

Ionic product of water:

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

1) Calculate the pH of 0.1 mol dm⁻³ NaOH:

$$[\text{NaOH}] = 0.1 \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$$

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{H}^+] = 1 \times 10^{-14} / 0.1$$

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

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

$$\text{pH} = -\log [1 \times 10^{-13}]$$

$$\text{pH} = 13.0$$

2) Calculate the pH of 0.005 mol dm⁻³ Mg(OH)₂

$$[\text{Mg(OH)}_2] = 0.005 \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = 0.005 \times 2$$

$$[\text{OH}^-] = 0.01$$

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{H}^+] = 1 \times 10^{-14} / 0.01$$

$$[\text{H}^+] = 1 \times 10^{-12}$$

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

$$\text{pH} = -\log [1 \times 10^{-12}]$$

$$\text{pH} = 12.0$$

b) Calculating the [OH⁻] of a strong base:

Examples:

1) Calculate the hydroxide concentration of a base with a pH = 10

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

$$[\text{H}^+] = 10^{-10}$$

$$[\text{H}^+] = 1 \times 10^{-10} \text{ mol dm}^{-3}$$

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 1 \times 10^{-10}$$

$$[\text{OH}^-] = 1 \times 10^{-12}$$

2) Calculate the hydroxide concentration of a base with a pH = 12.3

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

$$[\text{H}^+] = 10^{-12.3}$$

$$[\text{H}^+] = 5.01 \times 10^{-13} \text{ mol dm}^{-3}$$

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 5.01 \times 10^{-13}$$

$$[\text{OH}^-] = 0.02$$

3) Calculate the Barium hydroxide concentration with a pH = 13

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

$$[\text{H}^+] = 10^{-13}$$

$$[\text{H}^+] = 1 \times 10^{-13} \text{ mol dm}^{-3}$$

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 1 \times 10^{-13}$$

$$[\text{OH}^-] = 0.1$$

* Ba(OH)₂ has: 2 x [OH⁻] per [Ba(OH)₂]

$$[\text{Ba(OH)}_2] = 0.1 / 2$$

* Therefore divide by 2

$$[\text{Ba(OH)}_2] = 0.05$$

Questions:

1) Calculate the pH of the following strong bases:

a) $0.1 \text{ Mol dm}^{-3} \text{ NaOH}$

b) $0.01 \text{ Mol dm}^{-3} \text{ LiOH}$

c) $0.001 \text{ Mol dm}^{-3} \text{ KOH}$

d) $0.05 \text{ Mol dm}^{-3} \text{ Mg(OH)}_2$

e) $0.1 \text{ Mol dm}^{-3} \text{ Ga(OH)}_3$

f) $0.005 \text{ Mol dm}^{-3} \text{ Ca(OH)}_2$

2) Calculate the $[\text{OH}^-]$ of the following strong bases:

a) NaOH with a pH = 12

b) LiOH with a pH = 11

c) KOH with a pH = 10

d) Mg(OH)_2 with a pH = 12

e) Ga(OH)_3 with a pH = 12.6

f) Ca(OH)_2 with a pH = 14

3) Calculate the concentration of each of the strong bases above:

a) NaOH with a pH = 12

b) LiOH with a pH = 11

c) KOH with a pH = 10

d) Mg(OH)_2 with a pH = 12

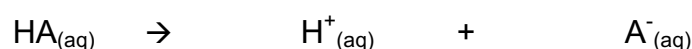
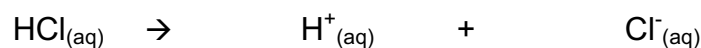
e) Ga(OH)_3 with a pH = 12.6

f) Ca(OH)_2 with a pH = 14

3) Weak acids

Strong acids:

- Remember, in aqueous solutions strong acids fully dissociate:

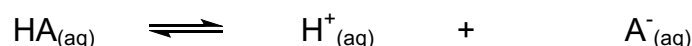


$$[\text{HA}_{(\text{aq})}] = [\text{H}^+_{(\text{aq})}]$$

- If you know the acid concentration, you know the hydrogen ion concentration.
- If you know the hydrogen ion concentration, you can calculate pH

Weak acids:

- This is not the case for weak acids:



- They partially dissociate.
- Approximately 0.5% of carboxylic acid molecules dissociate.

	$\text{CH}_3\text{COOH}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^+_{(\text{aq})}$	+	$\text{CH}_3\text{COO}^-_{(\text{aq})}$
Before dissociation - Moles:	1		0		0
After dissociation - Moles:	0.995		0.005		0.005

- This means:

$$[\text{HA}_{(\text{aq})}] \neq [\text{H}^+_{(\text{aq})}]$$

- This doesn't mean you can't calculate the $[\text{H}^+]$, you have to do it using an equilibrium expression:

The acid dissociation constant, K_a

- For ethanoic acid:



- An equilibrium expression can be written:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

- Notice that we used K_a for acid dissociation (equilibria) expressions.
- We used K_c when dealing with concentrations and K_p when dealing with pressures.
- Ethanoic acid has a $K_a = 1.7 \times 10^{-5} \text{ Mol dm}^{-3}$.

Units of K_a

- These are worked out in exactly the same way as for K_c :

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3}}$$

$$K_a = \text{mol dm}^{-3}$$

a) Calculating the pH for weak acids

Assumptions:

	$\text{CH}_3\text{COOH}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^+_{(\text{aq})}$	+	$\text{CH}_3\text{COO}^-_{(\text{aq})}$
Before dissociation - Moles:	1		0		0
After dissociation - Moles:	0.995		0.005		0.005

1) $[\text{CH}_3\text{COOH}]$ before dissociation \approx $[\text{CH}_3\text{COOH}]$ after dissociation:

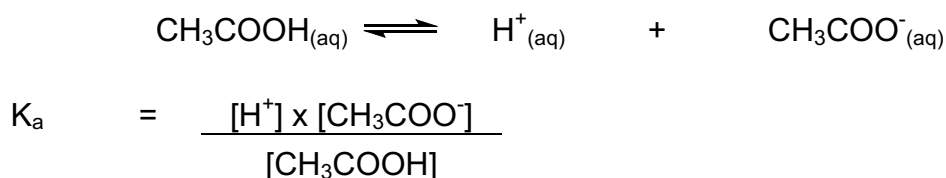
- Approximately 0.5% of acid molecules dissociate.
- This means that the change in concentration of the acid, CH_3COOH is negligible.

2) $[\text{H}^+] = [\text{A}^-]$

- For every acid molecule that dissociates, 1 H^+ and 1 CH_3COO^- are made.

The calculation

Step 1: Write the K_a expression



Step 2: Apply the assumptions

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

Step 3: Rearrange and put values in to calculate $[\text{H}^+]$:

$$[\text{H}^+]^2 = K_a \times [\text{CH}_3\text{COOH}]$$

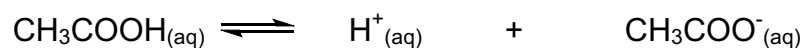
$$[\text{H}^+] = \sqrt{K_a \times [\text{CH}_3\text{COOH}]}$$

Step 4: Convert to pH:

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

Example: Calculate the pH of a 0.100 mol dm⁻³ ethanoic acid, $K_a = 1.7 \times 10^{-5}$ mol dm⁻³

Step 1: Write the K_a expression



$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Step2: Apply the assumptions

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

Step 3: Rearrange and put values in to calculate $[\text{H}^+]$:

$$[\text{H}^+]^2 = K_a \times [\text{CH}_3\text{COOH}]$$

$$[\text{H}^+] = \sqrt{K_a \times [\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \sqrt{1.7 \times 10^{-5} \times 0.1}$$

$$[\text{H}^+] = 1.304 \times 10^{-3}$$

Step 4: Convert to pH:

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

$$\text{pH} = -\log [1.304 \times 10^{-3}]$$

$$\text{pH} = 2.88$$

Summary:

Step 1: Write the K_a expression

Step2: Apply the assumptions

Step 3: Rearrange and put values in to calculate $[\text{H}^+]$:

Step 4: Convert to pH:

Questions:

1) Calculate the pH of a 0.05 mol dm^{-3} propanoic acid, $K_a = 1.3 \times 10^{-5} \text{ mol dm}^{-3}$

Step 1: Write the K_a expression

Step 2: Apply the assumptions

Step 3: Rearrange and put values in to calculate $[\text{H}^+]$:

Step 4: Convert to pH:

2) Calculate the pH of a $0.025 \text{ mol dm}^{-3}$ methanoic acid, $K_a = 1.8 \times 10^{-4} \text{ mol dm}^{-3}$

b) Calculating K_a for weak acids

The calculation:

Example: Calculate K_a for 0.03 mol dm^{-3} methanoic acid, $\text{pH} = 2.66$

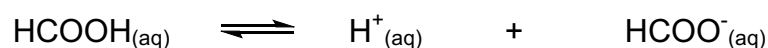
Step 1: Convert pH to $[\text{H}^+]$:

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

$$[\text{H}^+] = 10^{-2.66}$$

$$[\text{H}^+] = 2.19 \times 10^{-3}$$

Step 2: Write the K_a expression



$$K_a = \frac{[\text{H}^+] \times [\text{HCOO}^-]}{[\text{HCOOH}]}$$

Step 3: Apply the assumptions

$$K_a = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$$

Step 4: Put values in and calculate K_a :

$$K_a = \frac{[2.19 \times 10^{-3}]^2}{[0.03]}$$

$$K_a = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$$

Summary:

Step 1: Convert pH to $[\text{H}^+]$

Step 2: Write the K_a expression

Step 3: Apply the assumptions

Step 4: Put values in and calculate K_a :

Questions:

1) Calculate K_a for 0.01 mol dm^{-3} propanoic acid, $\text{pH} = 3.23$

Step 1: Convert pH to $[\text{H}^+]$:

Step 2: Write the K_a expression

Step 3: Apply the assumptions

Step 4: Put values in and calculate K_a :

2) Calculate K_a for $0.0025 \text{ mol dm}^{-3}$ methanoic acid, $\text{pH} = 4.56$

c) Calculating the concentration of weak acids

The calculation:

Example: Calculate the concentration of methanoic acid with a pH = 3 and K_a $1.8 \times 10^{-4} \text{ mol dm}^{-3}$

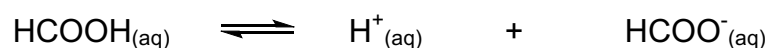
Step 1: Convert pH to $[H^+]$:

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

$$[H^+] = 10^{-3}$$

$$[H^+] = 1 \times 10^{-3}$$

Step 2: Write the K_a expression



$$K_a = \frac{[H^+] \times [HCOO^-]}{[HCOOH]}$$

Step 3: Apply the assumptions and rearrange

$$K_a = \frac{[H^+]^2}{[HCOOH]}$$

$$[HCOOH] = \frac{[H^+]^2}{K_a}$$

Step 4: Put values in and calculate $[HCOOH]$:

$$[HCOOH] = \frac{[1 \times 10^{-3}]^2}{1.8 \times 10^{-4}}$$

$$[HCOOH] = 0.005 \text{ mol dm}^{-3}$$

Summary:

Step 1: Convert pH to $[H^+]$

Step 2: Write the K_a expression

Step 3: Apply the assumptions and rearrange

Step 4: Put values in and calculate $[HCOOH]$:

Questions:

1) Calculate the concentration of ethanoic acid with a pH = 2.6 and K_a $1.7 \times 10^{-5} \text{ mol dm}^{-3}$

Step 1: Convert pH to $[H^+]$:

Step 2: Write the K_a expression

Step 3: Apply the assumptions and rearrange

Step 4: Put values in and calculate $[CH_3COOH]$:

2) Calculate the concentration of propanoic acid with a pH = 3.1 and K_a $1.3 \times 10^{-4} \text{ mol dm}^{-3}$

pK_a and the significance of K_a

- K_a is a measure of how much an acid dissociates.
- This is a measure then of the strength of an acid and values can vary from the very large → very small.
- Just like the pH scale it is more useful to compress (and flip) the scale.
- To keep it simple we use the same logarithmic scale that we used with pH.

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

$$pK_a = -\log_{10}[K_a]$$

- If it is a **strong acid** then it will dissociate a lot.
- This gives a large top number and a small bottom number.
- This will give a **large K_a** value, but a **small pK_a**

→ *Increasing acid strength* →

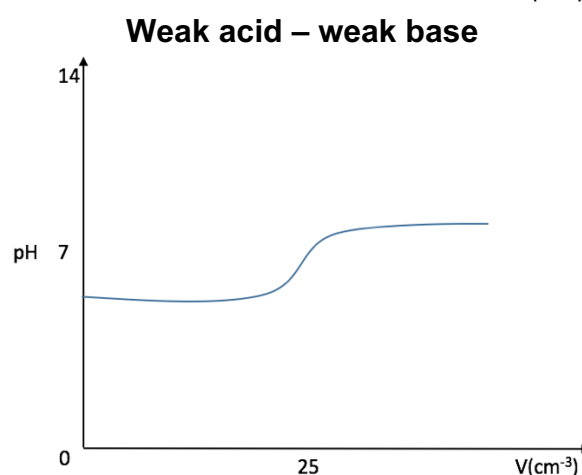
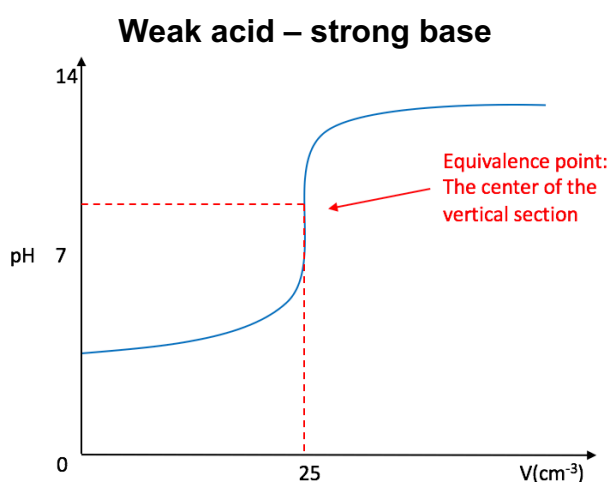
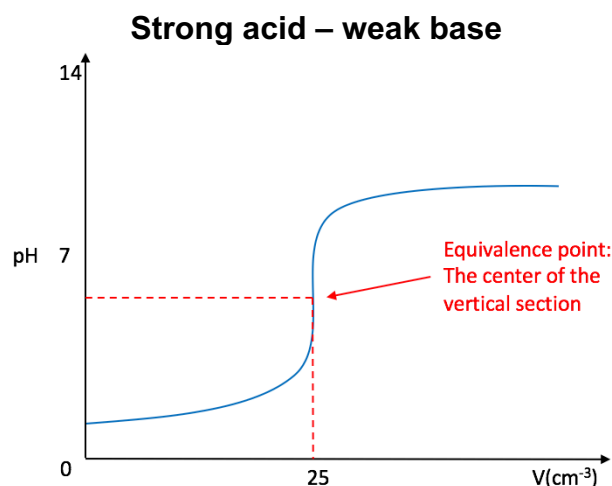
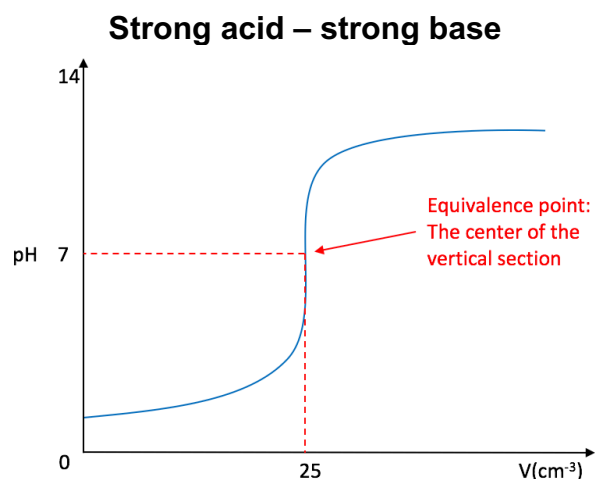
Acid	Benzoic acid	Ethanoic acid	Methanoic acid	Nitric acid
K _a	6.3 x 10 ⁻⁵	1.8 x 10 ⁻⁵	1.8 x 10 ⁻⁴	2.4 x 10 ¹
pK _a	4.2	4.7	3.7	-1.3

Neutralisation – Acid – base titration curves

Titration curves for AS chemistry

- During titrations you are measuring the exact volume of a known concentration with a known volume of another.
- This allows you to calculate the concentration of the other.
- **Acid - base titrations** plot **pH** against **volume** when an **acid** → **base** or a **base** → **acid**

Key features of titration curves - 50 cm³ of 0.1 mol dm⁻³ base added to 25 cm³ of acid:



Features of a neutralisation curve:

- **Starting pH** – determined by its concentration and whether it is a weak or strong acid (base).
- **Equivalence point** – Within a drop, the pH increases sharply from below 7 to above 7.
 - **Volume** of equivalence point
 - **pH** of equivalence point
 - **pH range** of equivalence point – indicator must change colour here
- **Final pH** – determined by its concentration and whether it is a weak or strong base (acid).

Acid – base combination	Example	Initial pH	Volume at equivalence point	pH at equivalence point	pH range of vertical section	Final pH
<i>Strong acid</i> <i>Strong base</i>	HCl NaOH	1	25	7	2 – 12	13
<i>Strong acid</i> <i>Weak base</i>	HCl NH ₃	1	25	5	2 – 8	10
<i>Weak acid</i> <i>Strong base</i>	CH ₃ COOH NaOH	3	25	9	6 – 12	13
<i>Weak acid</i> <i>Weak base</i>	CH ₃ COOH NH ₃	3	25	x	x	10

Indicators:

- Many dyes are affected by pH as they are themselves weak acids.
- This means that they will themselves be subject to shifts in their equilibrium with the addition of H⁺ or OH⁻.
- This will then correspond to a colour change at its own unique pH range

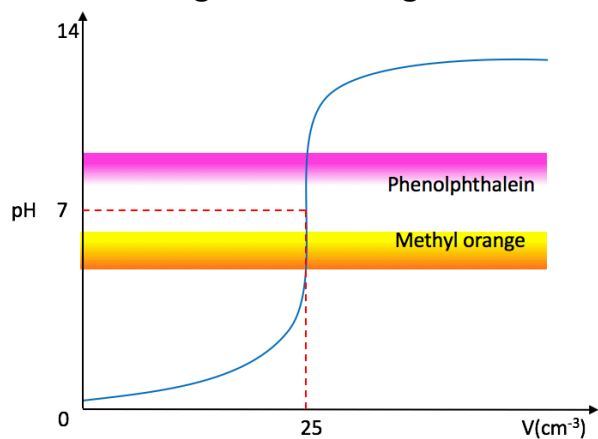


- Addition of an acid will move the equilibrium to the reactants. This shifts to the **RED**
- Addition of a base removes H⁺_(aq) which moves the equilibrium to the products.
- This shifts to the **YELLOW**
- **The end point** for chemical indicators is **in the middle** of its pH range.

Indicator and titration curves

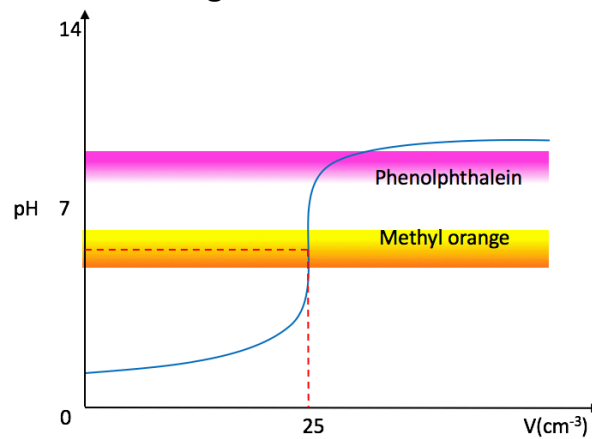
- **Equivalence point** – Center of the vertical section
- **End point** – Center of the colour change in indicator.
- The 2 must be as close as possible for a titration to give the correct molar ratio at neutralisation

Strong acid – strong base



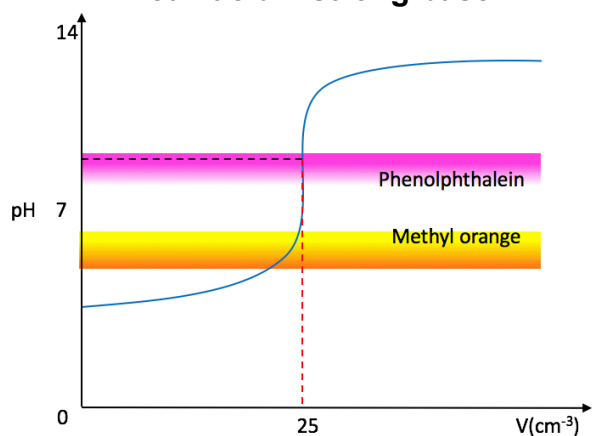
Both indicators suitable

Strong acid – weak base



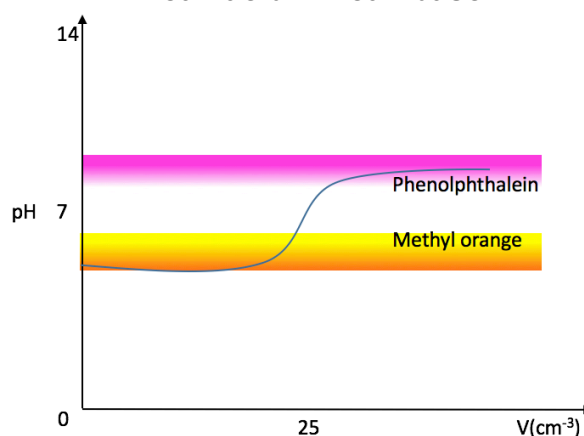
Methyl orange suitable

Weak acid – strong base



Phenolphthalein suitable

Weak acid – weak base



Neither suitable

Other indicators:

Indicator	pK _a	Colour in acid	pH range	Colour in alkali
Methyl orange	3.7	Red	3.2 – 4.4	Yellow
Methyl red	5.1	Red	4.2 – 6.3	Yellow
Phenol red	7.9	Yellow	6.8 – 8.4	Blue
Phenolphthalein	9.3	Colourless	8.2 – 10.0	Pink

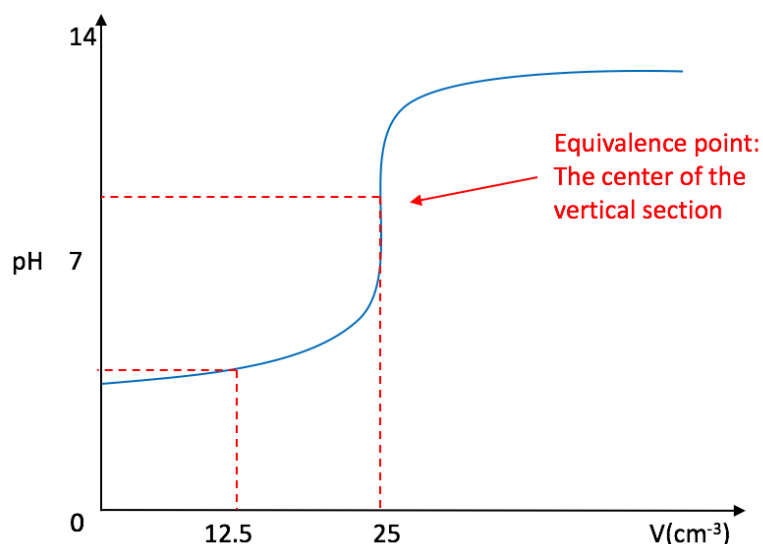
Questions:

NaOH was added to 25.0 cm³ of 0.10 mol dm⁻³ of ethanoic acid. The pH was recorded at regular intervals:

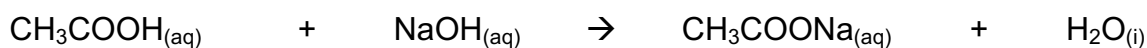
Vol of NaOH / cm ³	0.0	4.0	8.0	10.0	12.0	13.0	14.5	15.0	18.0	20.0
pH	2.8	3.5	4.4	5.0	5.4	6.2	11.4	12.0	12.3	12.4

- 1) Plot a pH curve using these results
- 2) Use the graph to read off the volume at the equivalence point and use it to calculate the concentration of the NaOH
- 3) State and explain which of the indicators at the top of the page you would use for this titration

Half equivalence point of a weak acid and K_a :



Consider the reaction:



- Instead of neutralising all of the acid we neutralised half of the acid.
- Half of the acid would be converted to the salt of the acid.
- This means we would have the same number of moles of acid as the salt of the acid:

$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COONa}]$$

- We know that the salt completely dissociates so:

$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$$

- Apply this to the acid dissociation expression:

$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = [\text{H}^+]$$

- Take '– log' of both sides (ie p)

$$\text{p}K_a = \text{pH}$$

At half neutralisation

$$\text{p}K_a = \text{pH}$$

4) Buffer solutions

Definitions:

Buffer solution:

A buffer solution minimises the change in pH with the small addition of acids or bases

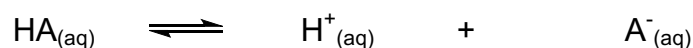
- There are 2 types of buffers - Acid and alkali buffers.
- It depends upon the pH you are trying to control.

How it works:

- Essentially it is an equilibrium that shifts to absorb or release H^+ or OH^- ions when they are added.
- In doing so it maintains the $[H^+]$ and $[OH^-]$

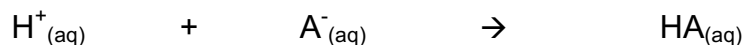
a) Acid buffers – pH < 7

- These are made using a weak acid:



➤ Adding acid, H^+

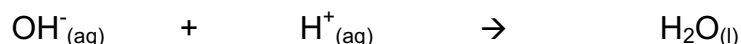
- The added H^+ ions react with A^- which shifts the equilibrium to the LHS:



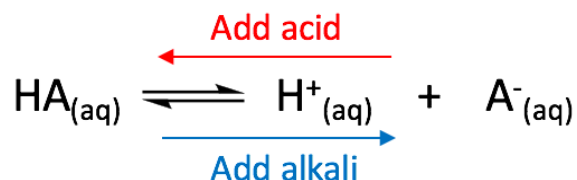
- The added H^+ ions are removed so the pH change is minimal.

➤ Adding alkali, OH^-

- The OH^- ions reacts with H^+ which shifts the equilibrium to the RHS:

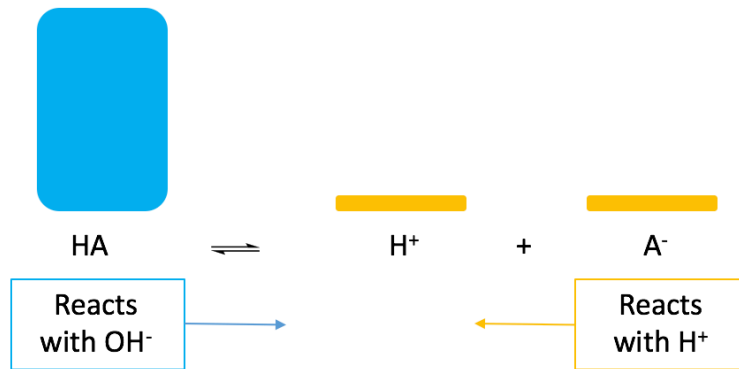


- The added OH^- ions are removed so the pH is change is minimal.



Problem:

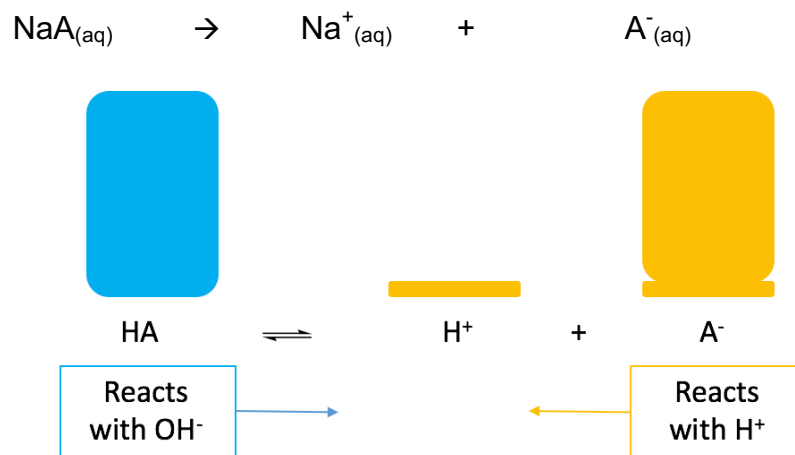
- This is a weak acid, the $[A^-]$ is very low.
- The A^- ions would soon be used up and no longer able to maintain the pH with a further addition of H^+ ions.



- More A^- is needed and this can be accomplished in one of 2 ways:

a) Adding the soluble salt of HA:

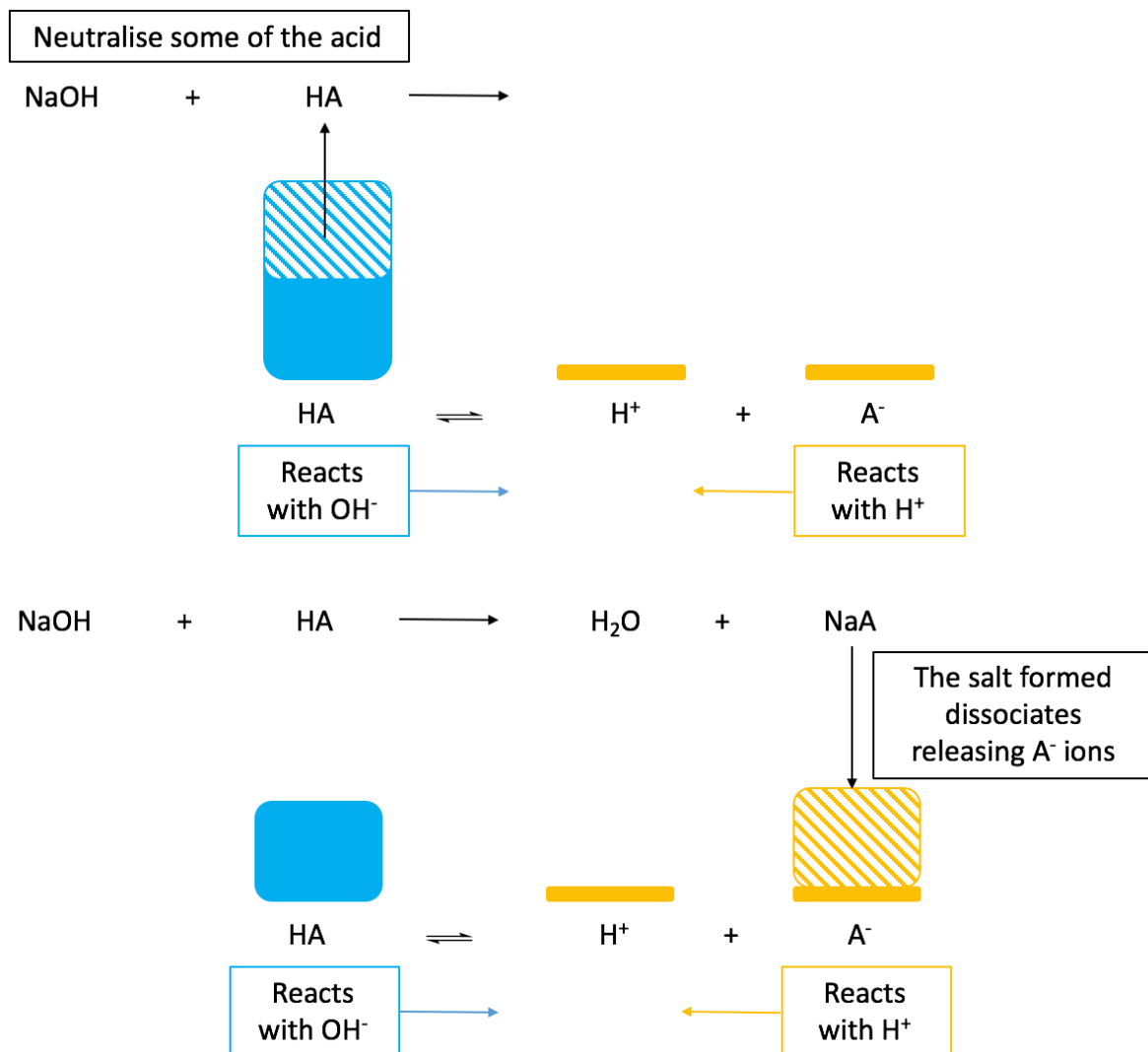
- This is done by the addition of NaA to the acid solution.
- As it is ionic, it dissociates completely:



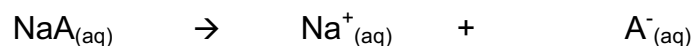
- This increases the $[A^-]$ allowing much more H^+ to be removed.

b) Neutralising some of the acid:

- Alternatively, $[A^-]$ can be increased by neutralising **some** of the acid:



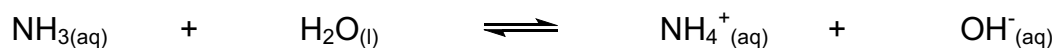
- Some of the acid is converted to the acid salt.
- This dissociates fully in solution:



- This increases the $[A^-]$ allowing much more H^+ to be removed.

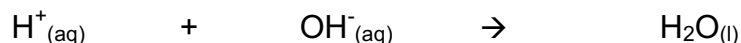
b) Basic buffers – pH > 7

- These are made using a weak base:



➤ Adding acid, H⁺

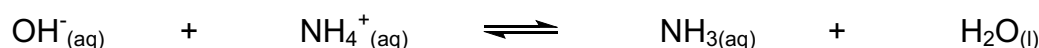
- The added H⁺ ions react with OH⁻ which shifts the equilibrium to the RHS:



- The added H⁺ ions are removed so the pH change is minimal.

➤ Adding alkali, OH⁻

- The added OH⁻ ions react with NH₄⁺ which shifts the equilibrium to the LHS:



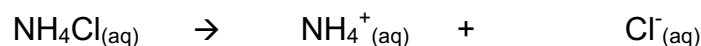
- The added OH⁻ ions are removed so the pH change is minimal.

Problem:

- Like the weak acid, this is a weak base, the [NH₄⁺] is very low.
- The NH₄⁺ ions would soon be used up and no longer able to maintain the pH with a further addition of OH⁻ ions.
- More NH₄⁺ is needed and this can be accomplished in one of 2 ways:

a) Adding the soluble salt of the weak base:

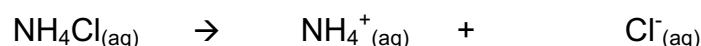
- This is done by the addition of NH₄Cl to the solution.
- As it is ionic, it dissociates completely:



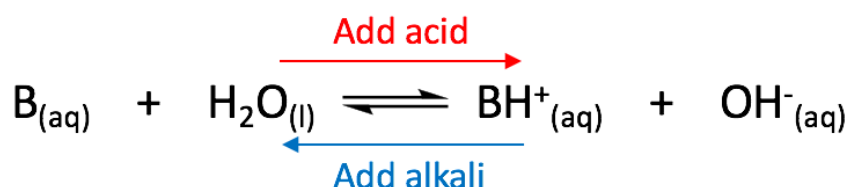
- This increases the [NH₄⁺] allowing much more OH⁻ to be removed.

b) Neutralising some of the base:

- Alternatively, [NH₄⁺] can be increased by neutralising **some** of the base:
- Some of the base is converted to the salt of the base.
- This dissociates fully in solution:

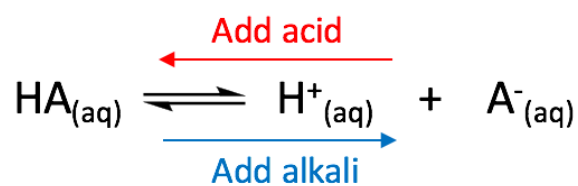


- This increases the [NH₄⁺] allowing much more H⁺ to be removed.

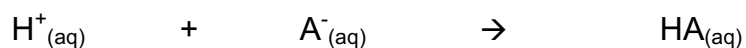


Summary

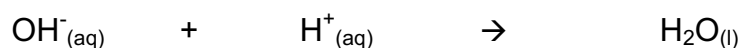
Weak acid buffer:



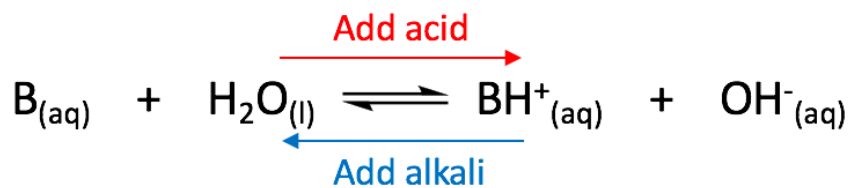
➤ **Adding acid, H⁺**



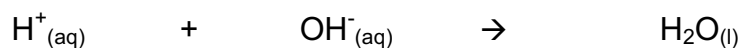
➤ **Adding alkali, OH⁻**



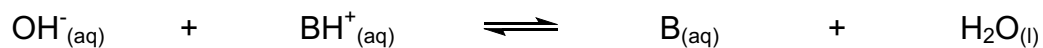
Weak basic buffer:



➤ **Adding acid, H⁺**



➤ **Adding alkali, OH⁻**



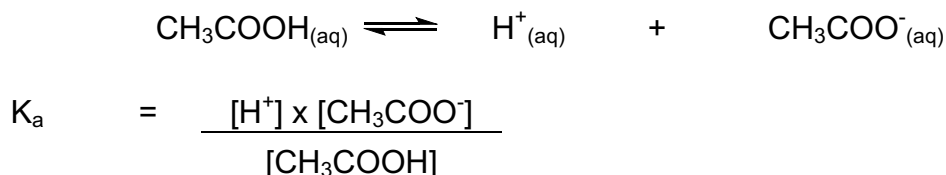
Calculations with buffer solutions

a) Calculating the pH for weak acids

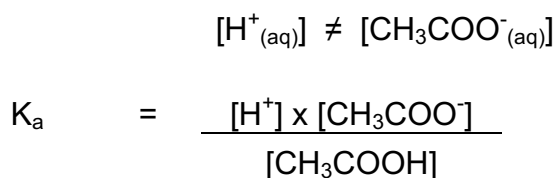
Example: A buffer solution contains $0.600 \text{ mol dm}^{-3}$ ethanoic acid and $0.800 \text{ mol dm}^{-3}$ sodium ethanoate. The equilibrium constant, K_a for ethanoic acid = $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the pH of the buffer solution:

Step 1: Write the K_a expression



** This assumption cannot be made as the salt of the acid increases the $[\text{CH}_3\text{COO}^-_{(\text{aq})}]$



Step 2: Rearrange and put values in to calculate $[\text{H}^+]$:

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{1.3 \times 10^{-5} \times 0.600}{0.800}$$

$$[\text{H}^+] = 9.75 \times 10^{-6}$$

Step 3: Convert to pH:

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

$$\text{pH} = -\log [9.785 \times 10^{-6}]$$

$$\text{pH} = 5.01$$

Summary:

Step 1: Write the K_a expression

Step 2: Rearrange and put values in to calculate $[\text{H}^+]$:

Step 3: Convert to pH:

Questions

- 1) A buffer solution contains $0.500 \text{ mol dm}^{-3}$ ethanoic acid and $0.300 \text{ mol dm}^{-3}$ sodium propanoate. The equilibrium constant, K_a for Ethanoic acid = $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the pH of the buffer solution:

Step 1: Write the K_a expression

Step 2: Rearrange and put values in to calculate $[\text{H}^+]$:

Step 3: Convert to pH:

[4.66]

- 2) A buffer solution contains $0.2500 \text{ mol dm}^{-3}$ methanoic acid and $0.400 \text{ mol dm}^{-3}$ sodium methanoate. The equilibrium constant, K_a for methanoic acid = $1.8 \times 10^{-4} \text{ mol dm}^{-3}$.

Calculate the pH of the buffer solution:

[3.95]

Other types of buffer calculation questions:

- 3) Calculate the pH of a buffer solution made when 4.10g of sodium ethanoate is added to 1dm³ of 0.10 mol dm⁻³ of ethanoic acid.

The equilibrium constant, K_a for ethanoic acid = 1.8×10^{-5} mol dm⁻³.

[4.44]

- 4) Calculate the mass of sodium ethanoate to be dissolved in 1dm³ of 0.10 mol dm⁻³ of ethanoic acid to make a buffer solution with a pH of 4.75

The equilibrium constant, K_a for ethanoic acid = 1.8×10^{-5} mol dm⁻³.

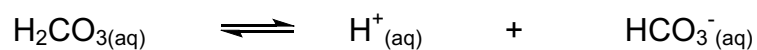
[8.28g]

5) Calculate the ratio of $[\text{HCOO}^-] : [\text{HCOOH}]$ of a buffer solution with $\text{pH} = 3.75$.

The equilibrium constant, K_a for methanoic acid = $1.8 \times 10^{-4} \text{ mol dm}^{-3}$.

[90:89]

6) Blood contains carbonic acid – hydrogen carbonate buffer to maintain the pH in blood.



Healthy blood has a pH of 7.40 with a hydrogen carbonate : carbonic acid ratio of 10.5 : 1

If the pH of a persons blood is 7.30, calculate the hydrogen carbonate : carbonic acid ratio in this persons blood (tip: use healthy blood to calculate K_a to use for the unhealthy blood)

[8.34:1]

7) Calculate the pH of a buffer solution made when 25 cm³ of 0.1 mol dm⁻³ NaOH is added to 25 cm³ of 0.2 mol dm⁻³ solution of ethanoic acid.

The equilibrium constant, K_a for ethanoic acid = 1.8×10^{-5} mol dm⁻³.

- Write the neutralisation reaction
- Calculate the number of moles of acid at the start
- Calculate the number of moles of sodium hydroxide added
- Calculate the number of moles of acid left after neutralisation
- Calculate the number of moles of the salt made after neutralisation (reacting ratios)
- Calculate the concentrations of the acid (after neutralisation)
- Calculate the concentration of the salt made (after neutralisation)
- Write the equilibrium reaction
- Write the equilibrium expression
- Put in the values to calculate $[H^+]$
- Calculate pH
- Use K_a in the question to calculate pK_a

[4.74]

- 8) Calculate the pH of a buffer solution made when 10 cm^3 of 0.01 mol dm^{-3} KOH is added to 40 cm^3 of 0.01 mol dm^{-3} solution of ethanoic acid.

The equilibrium constant, K_a for ethanoic acid = $1.8 \times 10^{-5} \text{ mol dm}^{-3}$.

[4.27]