

Topic 3 – Acids and Bases

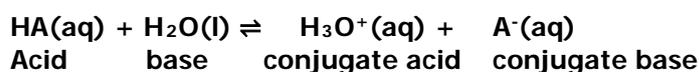
Revision Notes

1) Acids and Bases

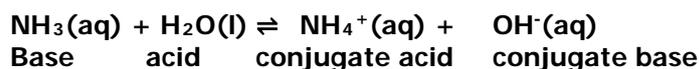
- The Bronsted-Lowry theory says that acids are proton donors (H^+ donors). Bases are proton acceptors.
- Strong acids and bases are fully dissociated (or ionised)
- Weak acids and bases are partially dissociated

a) Acid-base pairs

- Conjugate acid-base pairs are two species differing by H^+
- There is one member of the pair on each side of the equation
- For any weak acid, HA:



- In this reaction, A^- is the conjugate base of the acid HA because it is formed by loss of H^+ from HA
- In this example, H_3O^+ is the conjugate acid of the base H_2O because it is formed by the gain of H^+ by H_2O
- For a weak base, such as NH_3



2) Quantifying acid and base strength

- pH is a number that shows the strength of an acid or base
- $\text{pH} = -\log[H^+]$ and $[H^+] = 10^{-\text{pH}}$
- pH is always given to 2 decimal places
- $[H^+]$ deals with negative powers over a very wide range whereas the pH scale makes the numbers more manageable

a) pH of a strong acid

Example

Calculate the pH of $0.100 \text{ mol dm}^{-3}$ HCl

$$\begin{array}{l} [H^+] = 0.100 \\ \text{pH} = -\log[0.100] \\ = 1.00 \end{array}$$

b) pH of water

Water is very slightly dissociated: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

The equilibrium constant for this reaction is:

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

As $[\text{H}_2\text{O}]$ is little changed, we define a constant K_w , which is known as the ionic product of water

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

At 298K (25°C) K_w has the value of $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

For pure water, $[\text{H}^+] = [\text{OH}^-]$, so $K_w = [\text{H}^+]^2$ and $[\text{H}^+] = \sqrt{K_w}$

Example

At 318K, the value of K_w is $4.02 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the pH of water at this temperature and explain why the water is still neutral.

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_w} \\ &= \sqrt{4.02 \times 10^{-14}} \\ &= 2.01 \times 10^{-7} \text{ mol dm}^{-3} \\ \text{pH} &= -\log[\text{H}^+] \\ &= 6.70 \end{aligned}$$

Still neutral because $[\text{H}^+] = [\text{OH}^-]$

Source: AQA January 2006 paper

c) pH of a strong base

- The K_w expression is used to calculate the pH of a strong base

Calculate the pH of $0.100 \text{ mol dm}^{-3} \text{ NaOH}$ at 298K

$$\begin{aligned} [\text{OH}^-] &= 0.100 \\ [\text{H}^+] &= K_w/[\text{OH}^-] \\ &= 10^{-14}/0.100 \\ &= 10^{-13} \\ \text{pH} &= -\log[10^{-13}] \\ &= 13.00 \end{aligned}$$

d) pH of a weak acid

The weak acid HA dissociates as follows.



The equilibrium constant for the weak acid is:

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

K_a is a measure of the extent to which a weak acid is ionised. The larger the value of K_a the more the weak acid is ionised

When one mole of HA ionises, one mole of H^+ and one mole of A^- are produced i.e. $[\text{H}^+] = [\text{A}^-]$, so we can write:

$$K_a = [\text{H}^+]^2/[\text{HA}]$$

Re-arranging gives:

$$[\text{H}^+] = \sqrt{(K_a \times [\text{HA}])}$$

Calculate the pH of $0.100 \text{ mol dm}^{-3}$ chloroethanoic acid given that $K_a = 1.38 \times 10^{-3} \text{ mol dm}^{-3}$

$$\begin{aligned} [\text{H}^+] &= \sqrt{(K_a \times [\text{HA}])} \\ &= \sqrt{(1.38 \times 10^{-3} \times 0.100)} \\ &= \sqrt{(1.38 \times 10^{-4})} \\ &= 0.0117 \\ \text{pH} &= -\log[\text{H}^+] \\ &= 1.93 \end{aligned}$$

Source <http://www.chemsheets.co.uk/>

e) $\text{p}K_a$

- $\text{p}K_a = -\log(K_a)$ and $K_a = 10^{-\text{p}K_a}$
- As with pH, using $\text{p}K_a$ instead of K_a makes the numbers more manageable

Calculate the $\text{p}K_a$ of chloroethanoic acid

$$\begin{aligned} \text{From the previous example, } K_a &= 1.38 \times 10^{-3} \\ \text{p}K_a &= -\log(1.38 \times 10^{-3}) \\ &= 2.86 \end{aligned}$$

f) Diluting a strong acid or strong base

- For a diluted strong acid:

$$[\text{H}^+] = [\text{H}^+]_{\text{old}} \times \frac{\text{old volume}}{\text{New volume}}$$

- For a diluted strong base:

$$[\text{OH}^-] = [\text{OH}^-]_{\text{old}} \times \frac{\text{old volume}}{\text{New volume}}$$

Calculate the pH of the solution formed when 100 cm³ of water is added to 25 cm³ of 0.50 mol dm⁻³ KOH

$$[\text{OH}^-]_{\text{new}} = [\text{OH}^-]_{\text{old}} \times \frac{\text{old volume}}{\text{new volume}}$$

$$\text{New vol} = 25 + 100 \text{ cm}^3$$

$$[\text{OH}^-]_{\text{new}} = 0.50 \times \frac{25}{125}$$

$$= 0.10 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 1 \times 10^{-14} / 0.10$$

$$= 1 \times 10^{-13}$$

$$\text{pH} = 13.00$$

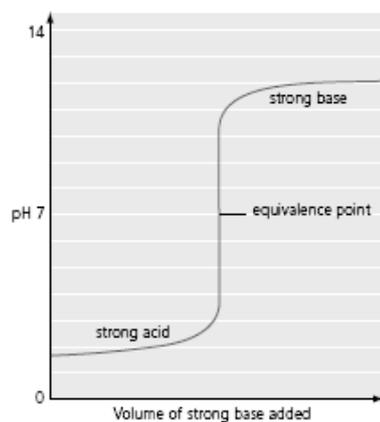
Source <http://www.chemsheets.co.uk/>

3) Acid-base titrations

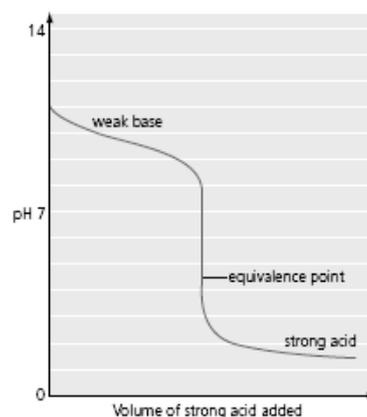
a) pH curves

- pH can be monitored during an acid-base titration and plotted against volume of reagent
- This produces a pH curve with a shape that depends on whether the acid and base are weak or strong

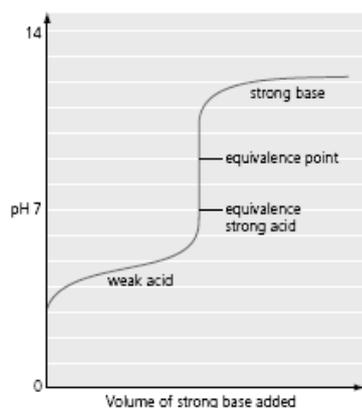
Strong acid-strong base



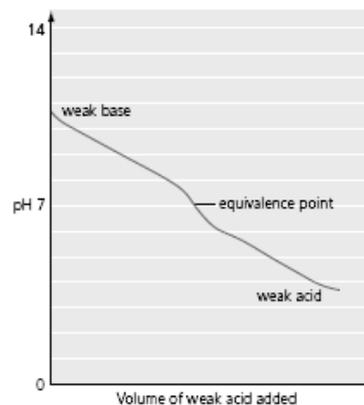
Weak base-strong acid



Weak acid-strong base



Weak base-weak acid



Source of these diagrams: CAMS Chemistry A2 Support Pack

- When selecting an indicator for a titration, the pH range in which the indicator changes colour must match the pH at the equivalence point of the titration
- Methyl orange - red in acid, pH range 3.1-4.4, yellow in alkali. Cannot be used for weak acids (vertical part of pH curve starts about pH 7)
- Phenolphthalein - colourless in acid, pH range 8.3-10.0, pink in alkali. Cannot be used for weak bases (vertical part of pH curve starts about pH 7)

b) Titration calculations

- Work out the moles of acid and base at the start
- Work out the excess moles of acid or base (the rest will be neutralised)
- For an excess of strong acid, work out the new $[H^+]$ and then the pH
- For an excess of strong base, work out the new $[OH^-]$ and then the pH
- With diprotic acids, like H_2SO_4 , work out $[H^+]$ rather than $[H_2SO_4]$. A similar adjustment is necessary for bases like $Sr(OH)_2$

Example – excess of strong base

Calculate the pH of the solution formed when 20 cm^3 of 0.10 mol dm^{-3} HCl is added to 30 cm^3 of 0.04 mol dm^{-3} NaOH

Moles HCl	= $0.10 \times 20/1000$
	= 0.0020 mol
Moles NaOH	= $0.04 \times 30/1000$
	= 0.0012 mol
Excess HCl	= $0.0020 - 0.0012$
	= 0.0008 mol
Total volume	= 50 cm^3
New $[H^+]$	= moles/volume
	= $0.0008/(50/1000)$
	= 0.016 mol dm^{-3}
pH	= $-\log(0.016)$
	= 1.80

Source <http://www.chemsheets.co.uk/>

4) Buffer solutions

- A buffer solution minimises pH changes on addition of a small amount of acid or base
- Buffer solutions are important for controlling pH in blood (so that enzymes are not denatured) and shampoos (so that eyes do not sting and skin is not damaged)

a) Acidic buffers

- An acidic buffer consists of a weak acid and the salt of a weak acid (e.g. ethanoic acid & sodium ethanoate). **The salt is fully ionised giving a high concentration of ethanoate ions.**
- For ethanoic acid/sodium ethanoate, the following equilibrium exists:



- If a small amount of acid is added, equilibrium will shift to the left to remove the added H^+ . The following reaction occurs: $CH_3COO^- + H^+ \rightarrow CH_3COOH$
- If a small amount of base is added, the OH^- will react with H^+ to form water. The equilibrium will shift to the right to replace the H^+ that has been removed. The following reaction occurs: $CH_3COOH \rightarrow CH_3COO^- + H^+$
- **In both cases the ratio $[CH_3COOH]/[CH_3COO^-]$ stays almost constant so the pH only changes by a small amount (see calculation below)**

b) Basic buffers

- A basic buffer consists of a weak base and the salt of a weak base (e.g. ammonia solution & ammonium chloride). As before, the salt is fully ionised giving a high concentration of ammonium ions.
- For ammonia/ammonium chloride, the following equilibrium exists:



- If a small amount of acid is added, the H^+ will react with ammonia to form ammonium ions i.e. the equilibrium will shift to the left to remove the added H^+
- If a small amount of base is added, the OH^- will react with H^+ to form water. Some ammonium ions will dissociate to replace the H^+ that has been removed
- **In both cases the ratio $[\text{NH}_4^+]/[\text{NH}_3]$ stays almost constant so the pH only changes by a small amount**

c) Calculating the pH of a buffer solution

- The pH of an acidic buffer can be calculated using the K_a expression for the weak acid e.g. for ethanoic acid/sodium ethanoate:

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

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

- The pH of a particular buffer depends on the value of K_a and the ratio of $[\text{CH}_3\text{COOH}]$ to $[\text{CH}_3\text{COO}^-]$
- This can be re-written as:

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

The volume cancels to leave
$$[\text{H}^+] = K_a \times \frac{\text{moles CH}_3\text{COOH}}{\text{Moles CH}_3\text{COO}^-}$$

The mole form of the equation is often more useful than the concentration version.

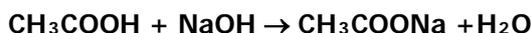
Example

Ethanoic acid is a weak acid with a K_a value of $1.74 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C . In a buffer solution, the concentration of ethanoic acid is $0.150 \text{ mol dm}^{-3}$ and the concentration of sodium ethanoate is $0.100 \text{ mol dm}^{-3}$. Calculate the pH of this buffer solution

$$\begin{aligned} [\text{H}^+] &= K_a \times [\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-] \\ &= 1.74 \times 10^{-5} \times 0.150/0.100 \\ &= 2.61 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.58 \end{aligned}$$

Source: AQA January 2005 paper

- A buffer solution can be formed by partial neutralisation of a weak acid. Some of the weak acid reacts with the added base to form a salt e.g.



- When a weak acid is half-neutralised, $[\text{Acid}] = [\text{Salt}]$ which means that $[\text{H}^+] = K_a$ and $\text{pH} = -\log[K_a]$ (i.e. $\text{pH} = \text{p}K_a$)

Example

A buffer solution is formed when 2.00g of sodium hydroxide are added to 1.00 dm³ of a 0.220 mol dm⁻³ solution of ethanoic acid. Calculate the pH of this buffer solution at 298K

$$\begin{aligned} \text{Moles NaOH used} &= 2.00/40.0 \\ &= 0.050 \text{ mol} \\ \text{Moles CH}_3\text{COOH at start} &= 0.220 \text{ mol} \\ \text{Moles CH}_3\text{COONa formed} &= 0.050 \text{ mol} \\ \text{Moles CH}_3\text{COOH left} &= 0.220 - 0.050 \\ &= 0.170 \text{ mol} \end{aligned}$$

In this case, converting moles to concentrations is unnecessary as the volumes cancel out

$$\begin{aligned} [\text{H}^+] &= K_a \times [\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-] \\ &= 1.74 \times 10^{-5} \times 0.170/0.050 \\ &= 5.916 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.23 \end{aligned}$$

Source: AQA January 2002 paper

Example – changes in pH of buffer solution

In a buffer solution, the concentration of ethanoic acid is 0.150 mol dm⁻³ and the concentration of sodium ethanoate is 0.100 mol dm⁻³. The acid dissociation constant for ethanoic acid, K_a , has a value of 1.74×10^{-5} mol dm⁻³ at 25 °C.

- (i) Calculate the pH of this buffer solution.

$$\begin{aligned} [\text{H}^+] &= K_a \times [\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-] \\ &= 1.74 \times 10^{-5} \times 0.150/0.100 \\ &= 2.61 \times 10^{-5} \\ \text{pH} &= 4.58 \end{aligned}$$

- (ii) A 10.0 cm³ portion of 1.00 mol dm⁻³ hydrochloric acid is added to 1000 cm³ of this buffer solution. Find the pH of this new solution.

$$\begin{aligned} \text{Original moles CH}_3\text{COOH} &= 0.150 \text{ mol} \\ \text{Original moles CH}_3\text{COO}^- &= 0.100 \text{ mol} \\ \text{Moles H}^+ \text{ added} &= 1.00 \times 10.0/1000 \end{aligned}$$

$$= 0.010 \text{ mol}$$



In this case, moles CH_3COO^- decreases by 0.010 and moles CH_3COOH increases by 0.010

New moles CH_3COOH = 0.160 mol

New moles CH_3COO^- = 0.090 mol

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

$$= 1.74 \times 10^{-5} \times \frac{0.160}{0.090}$$

$$= 3.90 \times 10^{-5}$$

New pH = 4.51

(iii) A 10.0 cm^3 portion of 1.00 mol dm^{-3} sodium hydroxide is added to 1000 cm^3 of the original buffer solution. Find the pH of this new solution.

Moles OH^- added = $1.00 \times 10.0/1000$

$$= 0.010 \text{ mol}$$



In this case, moles CH_3COOH decreases by 0.010 and moles CH_3COO^- increases by 0.010

New moles CH_3COOH = 0.140 mol

New moles CH_3COO^- = 0.110 mol

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

$$= 1.74 \times 10^{-5} \times \frac{0.140}{0.110}$$

$$= 2.21 \times 10^{-5}$$

New pH = 4.65