

## Topic 3 – Acids and Bases

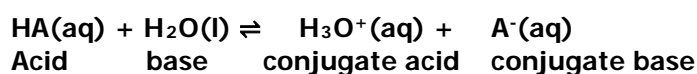
### Revision Notes

#### 1) Acids and Bases

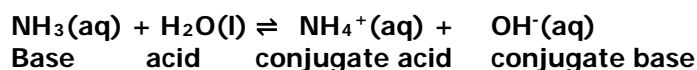
- The Bronsted-Lowry theory says that acids are proton donors (H<sup>+</sup> donors). Bases are proton acceptors.
- Strong acids and bases are fully dissociated (or ionised)
- Weak acids and bases are partially dissociated

##### a) Acid-base pairs

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



- In this reaction, A<sup>-</sup> is the conjugate base of the acid HA because it is formed by loss of H<sup>+</sup> from HA
- In this example, H<sub>3</sub>O<sup>+</sup> is the conjugate acid of the base H<sub>2</sub>O because it is formed by the gain of H<sup>+</sup> by H<sub>2</sub>O
- For a weak base, such as NH<sub>3</sub>



#### 2) Quantifying acid and base strength

- pH is a number that shows the strength of an acid or base
- $\text{pH} = -\log[\text{H}^+]$  and  $[\text{H}^+] = 10^{-\text{pH}}$
- pH is always given to 2 decimal places
- [H<sup>+</sup>] 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 mol dm<sup>-3</sup> HCl

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

**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  $\text{H}^+$  and one mole of  $\text{A}^-$  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 mol dm<sup>-3</sup> chloroethanoic acid given that  $K_a = 1.38 \times 10^{-3}$  mol dm<sup>-3</sup>

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

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

**e) pK<sub>a</sub>**

- $\text{p}K_a = -\log(K_a)$  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 cm<sup>3</sup> of water is added to 25 cm<sup>3</sup> of 0.50 mol dm<sup>-3</sup> KOH

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

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

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

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

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

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

$$\text{pH} = 13.00$$

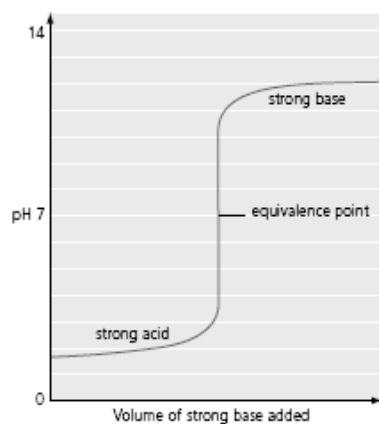
Source <http://www.chemsheets.co.uk/>

### 3) Acid-base titrations

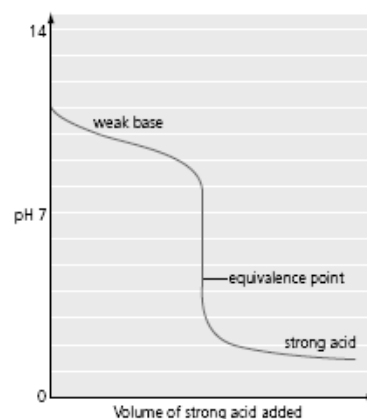
#### a) pH curves

- 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

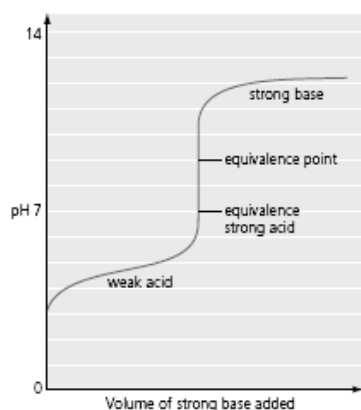
#### Strong acid-strong base



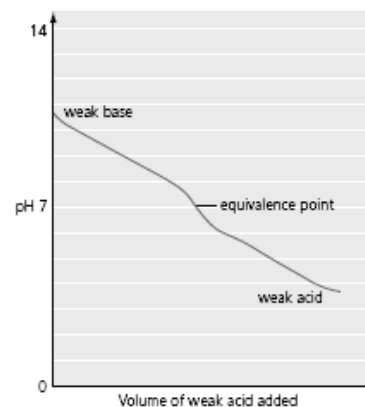
#### Weak base-strong acid



#### 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  $20\text{ cm}^3$  of  $0.10\text{ mol dm}^{-3}$  HCl is added to  $30\text{ cm}^3$  of  $0.04\text{ mol dm}^{-3}$  NaOH

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

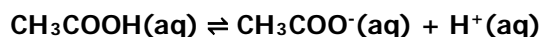
Source <http://www.chemsheets.co.uk/>

## 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  $\text{H}^+$  will react with ammonia to form ammonium ions i.e. the equilibrium will shift to the left to remove the added  $\text{H}^+$
- If a small amount of base is added, the  $\text{OH}^-$  will react with  $\text{H}^+$  to form water. Some ammonium ions will dissociate to replace the  $\text{H}^+$  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.

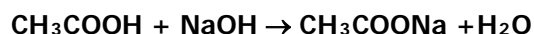
### Example

Ethanoic acid is a weak acid with a  $K_a$  value of  $1.74 \times 10^{-5} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . 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 dm<sup>3</sup> of a 0.220 mol dm<sup>-3</sup> solution of ethanoic acid. Calculate the pH of this buffer solution at 298K

Moles NaOH used	= 2.00/40.0
	= 0.050 mol
Moles CH <sub>3</sub> COOH at start	= 0.220 mol
Moles CH <sub>3</sub> COONa formed	= 0.050 mol
Moles CH <sub>3</sub> COOH left	= 0.220 - 0.050
	= 0.170 mol

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<sup>-3</sup> and the concentration of sodium ethanoate is 0.100 mol dm<sup>-3</sup>. The acid dissociation constant for ethanoic acid,  $K_a$ , has a value of  $1.74 \times 10^{-5} \text{ mol dm}^{-3}$  at 25 °C.

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

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

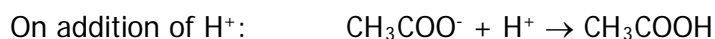
- (ii) A 10.0 cm<sup>3</sup> portion of 1.00 mol dm<sup>-3</sup> hydrochloric acid is added to 1000 cm<sup>3</sup> of this buffer solution. Find the pH of this new solution.

$$\begin{aligned} \text{Original moles CH}_3\text{COOH} &= 0.150 \text{ mol} \\ \text{Original moles CH}_3\text{COO}^- &= 0.100 \text{ mol} \end{aligned}$$

$$\text{Moles H}^+ \text{ added} = 1.00 \times 10.0/1000$$



$$= 0.010 \text{ mol}$$



In this case, moles  $\text{CH}_3\text{COO}^-$  decreases by 0.010 and moles  $\text{CH}_3\text{COOH}$  increases by 0.010

New moles  $\text{CH}_3\text{COOH}$  = 0.160 mol

New moles  $\text{CH}_3\text{COO}^-$  = 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  $10.0 \text{ cm}^3$  portion of  $1.00 \text{ mol dm}^{-3}$  sodium hydroxide is added to  $1000 \text{ cm}^3$  of the original buffer solution. Find the pH of this new solution.

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

$$= 0.010 \text{ mol}$$



In this case, moles  $\text{CH}_3\text{COOH}$  decreases by 0.010 and moles  $\text{CH}_3\text{COO}^-$  increases by 0.010

New moles  $\text{CH}_3\text{COOH}$  = 0.140 mol

New moles  $\text{CH}_3\text{COO}^-$  = 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