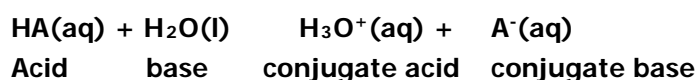


## Topic 3 – Acids, bases and buffers

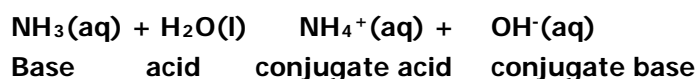
### Revision Notes

#### 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
- Conjugate acid-base pairs are two species differing by  $H^+$
- 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

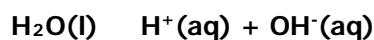
##### a) pH of a strong acid

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 a strong base

To calculate the pH of a strong base, we need to take advantage of the fact that water is very slightly dissociated.



The equilibrium constant for this reaction is:

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

As  $[H_2O]$  is little changed, we define a constant  $K_w$ , which is known as the ionic product of water

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

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

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

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

### c) pH of a weak acid

The weak acid HA dissociates as follows.



The equilibrium constant for the weak acid is:

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

$K_a$  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.  $[H^+] = [A^-]$ , so we can write:

$$K_a = [H^+]^2/[HA]$$

Re-arranging gives:

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

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

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

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

Percentage dissociation of a weak acid is  $[H^+]/[HA]$  i.e. hydrogen ion concentration/acid concentration

#### d) pH of water

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

##### 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.

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

Still neutral because  $[H^+] = [OH^-]$

Source: AQA January 2006 paper

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

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

Calculate the  $\text{pK}_a$  of chloroethanoic acid

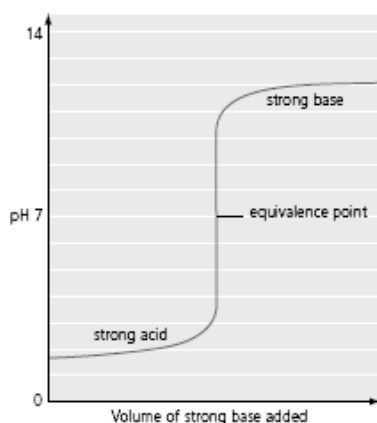
$$\begin{aligned} \text{From the previous example, } K_a &= 1.38 \times 10^{-3} \\ \text{pK}_a &= -\log(1.38 \times 10^{-3}) \\ &= 2.86 \end{aligned}$$

### 3) Acid-base titrations

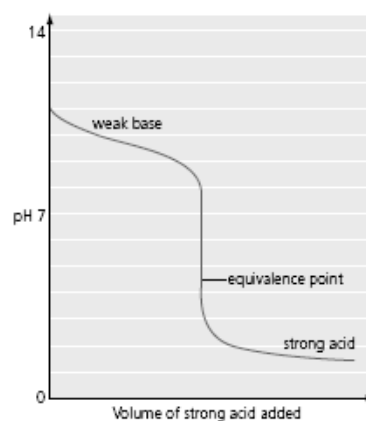
#### a) pH curves

- 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

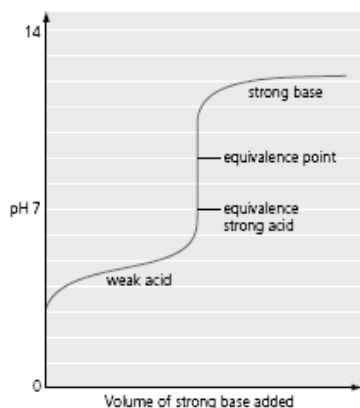
### Strong acid-strong base



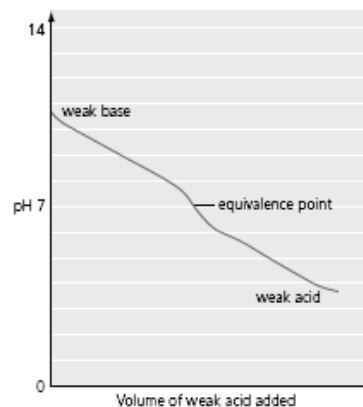
### Weak base-strong acid



### 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 vertical part of the relevant pH curve
- Phenolphthalein has a pH range of 8.2 to 10.0 so it is unsuitable for titrations involving weak bases
- Methyl orange has a pH range of 3.2 to 4.4 so it is unsuitable for titrations involving weak acids

### 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)
- Work out the new  $[H^+]$  or new  $[OH^-]$  and then the pH

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 cm <sup>3</sup>
New [H <sup>+</sup> ]	= moles/volume
	= 0.0008/(50/1000)
	= 0.016 mol dm <sup>-3</sup>
pH	= -log(0.016)
	= 1.80

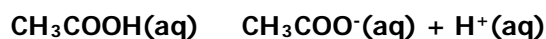
Source <http://www.chemsheets.co.uk/>

#### 4) Buffer solutions

- A buffer solution minimises pH changes on addition of an 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)
- 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<sup>+</sup>. The following reaction occurs: CH<sub>3</sub>COO<sup>-</sup> + H<sup>+</sup> → CH<sub>3</sub>COOH
- If a small amount of base is added, the OH<sup>-</sup> will react with H<sup>+</sup> to form water. The equilibrium will shift to the right to replace the H<sup>+</sup> that has been removed. The following reaction occurs: CH<sub>3</sub>COOH → CH<sub>3</sub>COO<sup>-</sup> + H<sup>+</sup>

##### b) Calculating the pH of a buffer solution

- The pH of an acidic buffer can be calculated using the K<sub>a</sub> 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:

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

Calculate the pH of a buffer solution containing equal volumes of 2.5 mol dm<sup>-3</sup> HCOONa and 1.0 mol dm<sup>-3</sup> HCOOH (K<sub>a</sub> = 1.6 x 10<sup>-4</sup> mol dm<sup>-3</sup>)

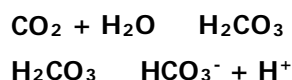
$$\begin{aligned} [\text{H}^+] &= K_a \times [\text{HCOOH}]/[\text{HCOONa}] \\ &= 1.6 \times 10^{-4} \times 1.0/2.5 \\ &= 6.4 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.19 \end{aligned}$$

Source: OCR June 2003 paper

- The pH of a particular buffer depends on the value of  $K_a$  and the ratio of  $[\text{CH}_3\text{COOH}]$  to  $[\text{CH}_3\text{COO}^-]$

#### d) pH of Blood

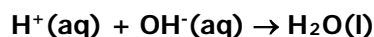
- The pH of blood is kept in the range 7.35-7.45
- This is achieved by dissolved carbon dioxide acting as a buffer solution
- The relevant equations are:



- $\text{H}_2\text{CO}_3$  is carbonic acid.  $\text{HCO}_3^-$  is the hydrogencarbonate ion
- If the blood pH is less than 7.35 (too acidic), more  $\text{CO}_2$  is breathed out. Both equilibria shift to the left to produce more  $\text{CO}_2$  and  $[\text{H}^+]$  is reduced
- If the blood pH is more than 7.45 (too alkaline), less  $\text{CO}_2$  is breathed out. Both equilibria shift to the right to remove  $\text{CO}_2$  and  $[\text{H}^+]$  is increased

### 5) Enthalpy of neutralisation

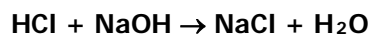
- Enthalpy of neutralisation is defined as the change in enthalpy that occurs when an acid and base undergo a neutralisation reaction to form one mole of water i.e.



- This is a calorimetry calculation e.g.

#### Example

50 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> hydrochloric acid was added to 50 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sodium hydroxide solution. The temperature rose by 6.8°C. Calculate the enthalpy of neutralisation for this reaction. Assume that the density of the solution is 1.00 g cm<sup>-3</sup>, the specific heat capacity of the solution is 4.18 J g<sup>-1</sup> K<sup>-1</sup>.



$m$  = mass of solution = total of acid and alkali = 100g

$$\begin{aligned} q &= -mc\Delta T/1000 \\ &= -100 \times 4.18 \times 6.8/1000 \\ &= -2.8424 \text{ kJ} \end{aligned}$$

$n$  = moles HCl = moles NaOH = 1.0 x 50/1000 = 0.05 mol

$$\begin{aligned} \Delta H &= q/n \\ &= -2.8424/0.05 \\ &= -56.8 \text{ kJ mol}^{-1} \end{aligned}$$

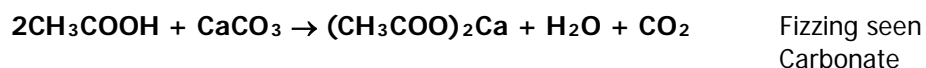
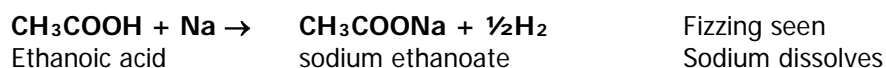
Source: [www.chemsheets.co.uk](http://www.chemsheets.co.uk)

## 6. Carboxylic acids

- Carboxylic acids contain the functional group –COOH on the end of a chain.
- They are weak acids (H<sup>+</sup> donors). The acidic H is in the –COOH group e.g.



- They are soluble in water because they can hydrogen bond to water molecules
- As they are acids they will react with metals, carbonates and bases:



dissolves



- Compounds containing 2 carboxylic acid groups are called dioic acids e.g. **HOOC-COOH** is ethanedioic acid and **HOOC-CH<sub>2</sub>-CH<sub>2</sub>-COOH** is butanedioic acid