

# ACIDS & BASES



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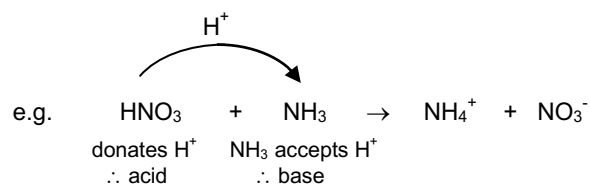
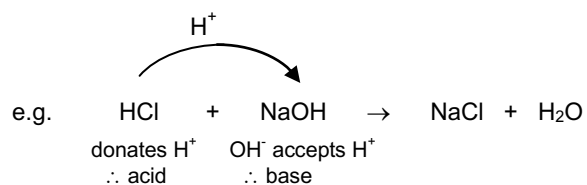


# SECTION 1 – Bronsted-Lowry acids & bases

Bronsted-Lowry acid = **proton donor** ( $H^+$  = proton)

Bronsted-Lowry base = **proton acceptor** ( $H^+$  = proton)

Bronsted-Lowry acid-base reaction = **reaction involving the transfer of a proton**



## TASK 1 – Bronsted-Lowry acids & bases

Identify the Bronsted-Lowry acid and base in each of the following reactions.

	acid	base
i) $\text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{OH}^- + \text{NH}_4^+$		
ii) $\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$		
iii) $\text{KOH} + \text{HCOOH} \rightarrow \text{HCOOK} + \text{H}_2\text{O}$		
iv) $\text{CH}_3\text{COOH} + \text{HCl} \rightarrow \text{CH}_3\text{COOH}_2^+ + \text{Cl}^-$		
v) $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$		
vi) $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$		
vii) $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$		
viii) $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$		

## SECTION 2 – pH of strong acids

### Number of protons released

Monoprotic acid = **acid that releases one H<sup>+</sup> ion per molecule**

e.g. HCl (hydrochloric acid), HNO<sub>3</sub> (nitric acid), CH<sub>3</sub>COOH (ethanoic acid)

Diprotic acid = **acid that releases two H<sup>+</sup> ions per molecule**

e.g. H<sub>2</sub>SO<sub>4</sub> (sulfuric acid), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (ethanedioic acid)

Moles of acid	Moles of H <sup>+</sup>
3 moles of HNO <sub>3</sub>	
2 moles of HCl	
4 moles of H <sub>2</sub> SO <sub>4</sub>	
0.3 moles of HNO <sub>3</sub>	
0.3 moles of H <sub>2</sub> SO <sub>4</sub>	

Moles of acid	Moles of H <sup>+</sup>
0.1 moles of H <sub>2</sub> SO <sub>4</sub>	
0.2 moles of HCl	
0.08 moles of HNO <sub>3</sub>	
0.08 moles of H <sub>2</sub> SO <sub>4</sub>	
0.35 moles of HCl	

### Definition of pH

Definition of pH

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

Useful rearrangement

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

**ALWAYS give pH to 2 DECIMAL PLACES**

[H <sup>+</sup> ]	0.00100		1.50		2.5 x 10 <sup>-4</sup>		4.5 x 10 <sup>-12</sup>		
pH		2.75		3.30		13.70		1.85	-0.70

### Examples – Calculating the pH of a strong acid

pH of 0.500 mol dm<sup>-3</sup> HNO<sub>3</sub>?  
 $[\text{H}^+] = 0.500$   
 $\text{pH} = -\log 0.500$   
 $\text{pH} = \underline{0.30}$

pH of 0.300 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>?  
 $[\text{H}^+] = 2 \times 0.300 = 0.600$  (diprotic acid!)  
 $\text{pH} = -\log 0.600$   
 $\text{pH} = \underline{0.22}$

[HCl] with pH 1.70?  
 $[\text{H}^+] = 10^{-1.70} = 0.0200$   
 $[\text{HCl}] = \underline{0.0200 \text{ mol dm}^{-3}}$

[H<sub>2</sub>SO<sub>4</sub>] with pH 1.30?  
 $[\text{H}^+] = 10^{-1.30} = 0.0501$   
 $[\text{H}_2\text{SO}_4] = 0.0501 / 2 = \underline{0.0251 \text{ mol dm}^{-3}}$

### **Examples – Dilution of a strong acid**

Calculate the pH of the solution formed when 100 cm<sup>3</sup> of water is added to 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HNO<sub>3</sub>.

$$[\text{H}^+] \text{ in original HNO}_3 \text{ solution} = 0.100$$

$$[\text{H}^+] \text{ in diluted solution} = 0.100 \times \frac{\text{old volume}}{\text{new volume}} = 0.100 \times \frac{50}{150} = 0.0333$$

$$\text{pH} = -\log 0.0333 = \underline{1.48}$$

Calculate the pH of the solution formed when 250 cm<sup>3</sup> of 0.300 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is made up to 2000 cm<sup>3</sup> solution with water.

$$[\text{H}^+] \text{ in original H}_2\text{SO}_4 \text{ solution} = 2 \times 0.300 = 0.600$$

$$[\text{H}^+] \text{ in diluted solution} = 0.600 \times \frac{\text{old volume}}{\text{new volume}} = 0.600 \times \frac{250}{2000} = 0.075$$

$$\text{pH} = -\log 0.075 = \underline{1.12}$$

## **TASK 2 – pH of strong acids**

**1** Calculate the pH of the following solutions.

- a) 0.2 mol dm<sup>-3</sup> HCl
- b) 0.05 mol dm<sup>-3</sup> HNO<sub>3</sub>
- c) 0.04 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>
- d) 2.00 mol dm<sup>-3</sup> HNO<sub>3</sub>

**2** Calculate the concentration of the following acids.

- a) HCl with pH 3.55
- b) H<sub>2</sub>SO<sub>4</sub> with pH 1.70
- c) HNO<sub>3</sub> with pH 1.30
- d) H<sub>2</sub>SO<sub>4</sub> with pH -0.50

**3** Calculate the pH of the solutions formed in the following way.

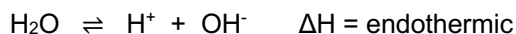
- a) addition of 250 cm<sup>3</sup> of water to 50 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> HNO<sub>3</sub>
- b) addition of 25 cm<sup>3</sup> of water to 100 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>
- c) adding water to 100 cm<sup>3</sup> of 2.00 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> to make 500 cm<sup>3</sup> of solution
- d) adding water to 25 cm<sup>3</sup> of 1.50 mol dm<sup>-3</sup> HCl to make 250 cm<sup>3</sup> of solution

**4** Calculate the pH of the following solutions.

- a) 10 g dm<sup>-3</sup> HCl
- b) 20 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>
- c) 50 g dm<sup>-3</sup> HNO<sub>3</sub>
- d) 100 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

## SECTION 3 – The ionic product of water, $K_w$

### The ionic product of water ( $K_w$ )



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

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

As  $[\text{H}_2\text{O}]$  is very much greater than  $[\text{H}^+]$  and  $[\text{OH}^-]$ , then  $[\text{H}_2\text{O}]$  is effectively a constant number

$$\therefore K_c [\text{H}_2\text{O}] = \text{a constant} = K_w$$

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

### The effect of temperature on the pH of water and the neutrality of water

As the temperature increases, the equilibrium moves right to oppose the increase in temperature

$\therefore [\text{H}^+]$  and  $[\text{OH}^-]$  increase

$\therefore K_w$  increases and  $\therefore$  pH decreases

However, the water is still neutral as  $[\text{H}^+] = [\text{OH}^-]$  (and the definition of neutral is  $[\text{H}^+] = [\text{OH}^-]$ )

### Calculating the pH of water

In pure water,  $[\text{H}^+] = [\text{OH}^-]$

$$\therefore K_w = [\text{H}^+]^2$$

$$\therefore [\text{H}^+] = \sqrt{K_w}$$

e.g. calculate the pH of water at 40°C when  $K_w = 2.09 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$K_w = [\text{H}^+]^2$$

$$\therefore [\text{H}^+] = \sqrt{K_w} = \sqrt{(2.09 \times 10^{-14})} = 1.45 \times 10^{-7}$$

$$\therefore \text{pH} = -\log(1.45 \times 10^{-7}) = \underline{\underline{6.84}}$$

## SECTION 4 – The pH of strong bases

### Examples – Calculating the pH of a strong base

pH of 0.200 mol dm<sup>-3</sup> NaOH?      [OH<sup>-</sup>] = 0.200  
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.200} = 5 \times 10^{-14}$$
$$pH = -\log[H^+] = -\log(5 \times 10^{-14}) = \underline{13.30}$$

pH of 0.0500 mol dm<sup>-3</sup> Ba(OH)<sub>2</sub>?      [OH<sup>-</sup>] = 2 x 0.0500 = 0.100  
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.100} = 1 \times 10^{-13}$$
$$pH = -\log[H^+] = -\log(1 \times 10^{-13}) = \underline{13.00}$$

[KOH] with pH 12.70?      [H<sup>+</sup>] = 10<sup>-pH</sup> = 10<sup>-12.70</sup> = 2.00 x 10<sup>-13</sup>  
$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2.00 \times 10^{-13}} = 0.05$$
$$[KOH] = \underline{0.05 \text{ mol dm}^{-3}}$$

[Ba(OH)<sub>2</sub>] with pH 13.30?      [H<sup>+</sup>] = 10<sup>-pH</sup> = 10<sup>-13.30</sup> = 5.01 x 10<sup>-14</sup>  
$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{5.01 \times 10^{-14}} = 0.200$$
$$[Ba(OH)_2] = \underline{0.100 \text{ mol dm}^{-3}}$$

### Examples – Dilution of a strong base

Calculate the pH of the solution formed when 50 cm<sup>3</sup> of water is added to 100 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> NaOH.

[OH<sup>-</sup>] in original NaOH solution = 0.200  
[OH<sup>-</sup>] in diluted solution = 0.200 x  $\frac{\text{old volume}}{\text{new volume}}$  = 0.200 x  $\frac{100}{150}$  = 0.1333  
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.1333} = 7.50 \times 10^{-14}$$
$$pH = -\log(7.50 \times 10^{-14}) = \underline{13.12}$$

Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.250 mol dm<sup>-3</sup> KOH is made up to 250 cm<sup>3</sup> solution with water.

[OH<sup>-</sup>] in original KOH solution = 0.250  
[OH<sup>-</sup>] in diluted solution = 0.250 x  $\frac{\text{old volume}}{\text{new volume}}$  = 0.250 x  $\frac{50}{250}$  = 0.0500  
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.0500} = 2.00 \times 10^{-13}$$
$$pH = -\log(2.00 \times 10^{-13}) = \underline{12.70}$$

### TASK 3 – pH of strong bases

- 1** Calculate the pH of the following solutions.
  - a)  $0.15 \text{ mol dm}^{-3} \text{ KOH}$
  - b)  $0.05 \text{ mol dm}^{-3} \text{ NaOH}$
  - c)  $0.20 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$
- 2** Calculate the concentration of the following bases.
  - a) NaOH with pH 14.30
  - b)  $\text{Ba(OH)}_2$  with pH 12.50
  - c) KOH with pH 13.70
- 3** Calculate the pH of the solutions formed in the following way.
  - a) addition of  $100 \text{ cm}^3$  of water to  $25 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ NaOH}$
  - b) addition of  $25 \text{ cm}^3$  of water to  $100 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$
  - c) adding water to  $100 \text{ cm}^3$  of  $1.00 \text{ mol dm}^{-3} \text{ KOH}$  to make  $1 \text{ dm}^3$  of solution
- 4** Calculate the pH of the following solutions.
  - a)  $20 \text{ g dm}^{-3} \text{ NaOH}$
  - b)  $100 \text{ g dm}^{-3} \text{ KOH}$
  - c)  $1 \text{ g dm}^{-3} \text{ Sr(OH)}_2$

## SECTION 5 – The pH of mixtures of strong acids and strong bases

- 1) Calculate moles  $\text{H}^+$
- 2) Calculate moles  $\text{OH}^-$
- 3) Calculate moles XS  $\text{H}^+$  or  $\text{OH}^-$
- 4) Calculate XS  $[\text{H}^+]$  or XS  $[\text{OH}^-]$
- 5) Calculate pH

### **Example – with excess $\text{H}^+$**

Calculate the pH of the solution formed when  $50 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  is added to  $25 \text{ cm}^3$  of  $0.150 \text{ mol dm}^{-3} \text{ NaOH}$ .

$$\text{mol H}^+ = 2 \times \frac{50}{1000} \times 0.100 = 0.0100$$

$$\text{mol OH}^- = \frac{25}{1000} \times 0.150 = 0.00375$$

$$\therefore \text{XS mol H}^+ = 0.0100 - 0.00375 = 0.00625$$

$$\therefore \text{XS } [\text{H}^+] = \frac{0.00625}{\frac{75}{1000}} = 0.0833$$

$$\text{pH} = -\log(0.0833) = \underline{1.08}$$

### **Example – with excess $\text{OH}^-$**

Calculate the pH of the solution formed when  $25 \text{ cm}^3$  of  $0.250 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  is added to  $100 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3} \text{ NaOH}$ .

$$\text{mol H}^+ = 2 \times \frac{25}{1000} \times 0.250 = 0.0125$$

$$\text{mol OH}^- = \frac{100}{1000} \times 0.200 = 0.0200$$

$$\therefore \text{XS mol OH}^- = 0.0200 - 0.0125 = 0.0075$$

$$\therefore \text{XS } [\text{OH}^-] = \frac{0.0075}{\frac{125}{1000}} = 0.0600$$

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.0600} = 1.67 \times 10^{-13}$$

$$\text{pH} = -\log(1.67 \times 10^{-13}) = \underline{12.78}$$

## TASK 4 – pH of mixtures of strong acids and strong bases

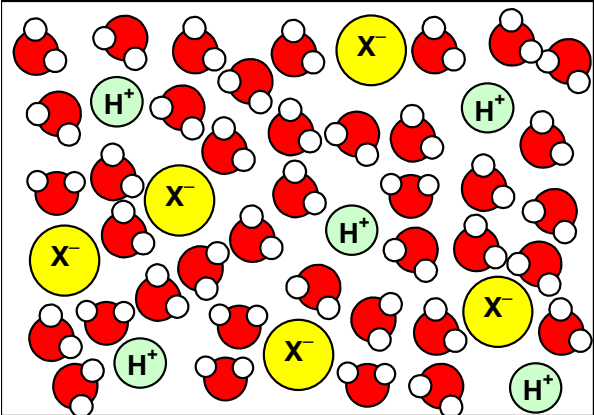
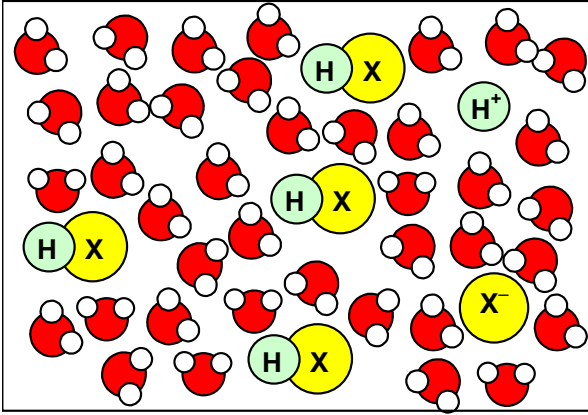
- 1** Calculate the pH of the solution formed when 20 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HNO<sub>3</sub> is added to 30 cm<sup>3</sup> of 0.050 mol dm<sup>-3</sup> KOH.
- 2** Calculate the pH of the solution formed when 25 cm<sup>3</sup> of 0.150 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is added to 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH.
- 3** Calculate the pH of the solution formed when 100 cm<sup>3</sup> of 0.050 mol dm<sup>-3</sup> HCl is added to 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> KOH.
- 4** Calculate the pH of the solution formed when 10 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is added to 25 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> NaOH.
- 5** Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.250 mol dm<sup>-3</sup> HNO<sub>3</sub> is added to 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> Ba(OH)<sub>2</sub>.
- 6** Calculate the pH **change** to 100 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> HCl solution in a flask if 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH is added.
- 7** Calculate the pH **change** to 50 cm<sup>3</sup> of 0.150 mol dm<sup>-3</sup> KOH solution in a flask if 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is added.

## TASK 5 – A variety of pH calculations so far

- 1** Calculate the pH of the following solutions:  
a) 0.150 mol dm<sup>-3</sup> Ba(OH)<sub>2</sub>                      c) 1.500 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>  
b) 0.200 mol dm<sup>-3</sup> HNO<sub>3</sub>                      d) 0.0500 mol dm<sup>-3</sup> NaOH
- 2** a) Calculate the pH of water at 50°C when  $K_w = 5.48 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .  
b) is the water neutral? Explain your answer.
- 3** a) 20 cm<sup>3</sup> of 1.0 M H<sub>2</sub>SO<sub>4</sub> with water added to make the volume up to 100 cm<sup>3</sup>.  
b) 50 cm<sup>3</sup> of 0.05 M KOH with 200 cm<sup>3</sup> of water added.
- 4** a) Calculate the pH of the solution formed when 100 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is added to 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> NaOH.  
b) Calculate the pH of the solution formed when 25 cm<sup>3</sup> of 0.250 mol dm<sup>-3</sup> HCl is added to 15 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> KOH.
- 5** Calculate the pH of the solution formed when 3.5 g of impure sodium hydroxide (98.7 % purity) is dissolved in water and made up to 100 cm<sup>3</sup>, and then 25 cm<sup>3</sup> of 0.35 mol dm<sup>-3</sup> diprotic acid is added.

## SECTION 6 – Weak acids

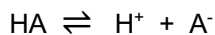
### What is the difference between strong and weak acids?

Strong acid	Weak acid
all the molecules break apart to form ions	only a small fraction of the molecules break apart to form ions
	
$\text{HX} \rightarrow \text{H}^+ + \text{X}^-$	$\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$

### Common acids and bases

	ACIDS		BASES	
	Strong	Weak	Strong	Weak
Monoprotic / basic	HCl hydrochloric acid HNO <sub>3</sub> nitric acid	carboxylic acids (e.g. ethanoic acid)	NaOH sodium hydroxide KOH potassium hydroxide	NH <sub>3</sub> ammonia
Diprotic / basic	H <sub>2</sub> SO <sub>4</sub> sulfuric acid		Ba(OH) <sub>2</sub> barium hydroxide	

### The acid dissociation constant, $K_a$



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

$$\text{p}K_a = -\log K_a$$

$$K_a = 10^{-\text{p}K_a}$$

These expressions hold for weak acids at all times

#### Note

- $K_a$  – has units  $\text{mol dm}^{-3}$
- $K_a$  – the bigger the value, the stronger the acid
- $\text{p}K_a$  – the smaller the value, the stronger the acid

In a solution of a weak acid in water, with nothing else added:

- a)  $[H^+] = [A^-]$
- b)  $[HA] \approx [HA]_{\text{initial}}$  (i.e. the concentration of HA at equilibrium is virtually the same as it was before any of it dissociated as so little dissociates, e.g. in a  $0.100 \text{ mol dm}^{-3}$  solution of HA, there is virtually  $0.100 \text{ mol dm}^{-3}$  of HA)

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

This expression ONLY holds for weak acids in aqueous solution with nothing else added

**Example – finding the pH of a weak acid**

Calculate the pH  $0.100 \text{ mol dm}^{-3}$  propanoic acid ( $pK_a = 4.87$ ).

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

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

$$[H^+] = \sqrt{K_a [HA]} = \sqrt{(10^{-4.87} \times 0.100)} = 1.16 \times 10^{-3}$$

$$pH = -\log(1.16 \times 10^{-3}) = \underline{2.94}$$

**Example – finding the concentration of a weak acid from pH**

Calculate the concentration of a solution of methanoic acid with pH 4.02 ( $K_a = 1.35 \times 10^{-5} \text{ mol dm}^{-3}$ ).

$$[H^+] = 10^{-4.02} = 9.55 \times 10^{-5}$$

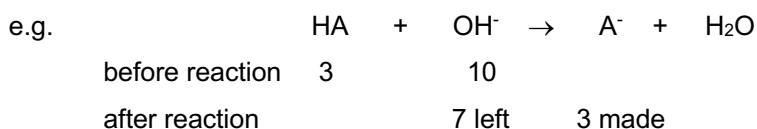
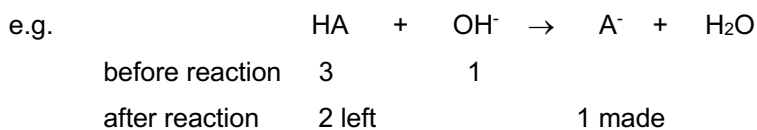
$$[HA] = \frac{[H^+]^2}{K_a} = \frac{(9.55 \times 10^{-5})^2}{1.35 \times 10^{-5}} = 6.76 \times 10^{-4} \text{ mol dm}^{-3}$$

## TASK 6 – The pH of weak acids

- 1 Calculate the pH of the following weak acids:
  - a)  $0.150 \text{ mol dm}^{-3}$  benenecarboxylic acid ( $pK_a = 4.20$ )
  - b)  $0.200 \text{ mol dm}^{-3}$  butanoic acid ( $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$ )
  - c)  $1.00 \text{ mol dm}^{-3}$  methanoic acid ( $K_a = 1.78 \times 10^{-4} \text{ mol dm}^{-3}$ )
- 2 Calculate the concentration of the following weak acids.
  - a) ethanoic acid with pH 4.53 ( $K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$ )
  - b) pentanoic acid with pH 3.56 ( $pK_a = 4.86$ )
- 3
  - a) Which is the stronger acid, ethanoic acid ( $pK_a = 4.76$ ) or propanoic acid ( $pK_a = 4.87$ )?
  - b) Which is the stronger acid, propanoic acid ( $K_a = 1.35 \times 10^{-5} \text{ mol dm}^{-3}$ ) or propenoic acid ( $K_a = 5.50 \times 10^{-5} \text{ mol dm}^{-3}$ )?
- 4 Calculate the  $K_a$  value for phenylethanoic acid given that a  $0.100 \text{ mol dm}^{-3}$  solution has a pH of 2.66.

## Reactions between weak acids and strong bases

When a weak acid reacts with a strong base, for every mole of  $\text{OH}^-$  added, one mole of HA is used up and one mole of  $\text{A}^-$  is formed.



### TASK 7 – Reactions of weak acids

When the following weak acids react with strong bases, calculate

- the moles of HA left after reaction
- the moles of  $\text{OH}^-$  left after reaction
- the moles of  $\text{A}^-$  formed in the reaction

- 1 4 moles of HA with 2.5 moles of NaOH
- 2 6 moles of HA with 1.3 moles of  $\text{Ba}(\text{OH})_2$
- 3 0.15 moles of HA with 0.25 moles of KOH
- 4 0.30 moles of HA with 0.15 moles of NaOH
- 5 100  $\text{cm}^3$  of 0.100  $\text{mol dm}^{-3}$  HA with 50  $\text{cm}^3$  0.050  $\text{mol dm}^{-3}$  NaOH
- 6 25  $\text{cm}^3$  of 0.500  $\text{mol dm}^{-3}$  HA with 40  $\text{cm}^3$  of 1.0  $\text{mol dm}^{-3}$  KOH
- 7 10  $\text{cm}^3$  of 0.100  $\text{mol dm}^{-3}$  HA with 10  $\text{cm}^3$  of 0.080  $\text{mol dm}^{-3}$  NaOH

## Finding the pH in reactions between weak acids and strong bases

When a weak acid reacts with a strong base, for every mole of  $\text{OH}^-$  added, one mole of HA is used up and one mole of  $\text{A}^-$  is formed.

- 1) Calculate moles HA (it is still HA and not  $\text{H}^+$  as it is a weak acid)
- 2) Calculate moles  $\text{OH}^-$
- 3) Calculate moles XS HA or  $\text{OH}^-$

#### **If XS HA**

- 4) Calculate moles HA left and  $\text{A}^-$  formed
- 5) Calculate  $[\text{HA}]$  leftover and  $[\text{A}^-]$  formed
- 6) Use  $K_a$  to find  $[\text{H}^+]$
- 7) Find pH

#### **If XS $\text{OH}^-$**

- 4) Calculate  $[\text{OH}^-]$
- 5) Use  $K_w$  to find  $[\text{H}^+]$
- 6) Find pH

#### **If mol HA = $\text{OH}^-$**

- 4)  $\text{pH} = \text{p}K_a$  of weak acid

*Note* – if there is XS base, then in terms of working out the pH it is irrelevant whether it was a strong or weak acid as it has all reacted!

### Example – with excess OH<sup>-</sup>

Calculate the pH of the solution formed when 30 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> ethanoic acid (pK<sub>a</sub> = 4.76) is added to 100 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH.

$$\text{mol HA} = \frac{30}{1000} \times 0.200 = 0.00600$$

$$\text{mol OH}^- = \frac{100}{1000} \times 0.100 = 0.0100 \quad \therefore \text{OH}^- \text{ is in XS}$$

$$\text{XS mol OH}^- = 0.0100 - 0.00600 = 0.00400$$

$$\therefore \text{XS [OH}^-] = \frac{0.00400}{\frac{130}{1000}} = 0.0308$$

$$\therefore \text{XS [H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.0308} = 3.25 \times 10^{-13}$$

$$\text{pH} = -\log(3.25 \times 10^{-13}) = \underline{12.49}$$

### Example – with excess HA

Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> ethanoic acid (pK<sub>a</sub> = 4.76) is added to 75 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> NaOH.

$$\text{mol HA} = \frac{50}{1000} \times 0.500 = 0.0250$$

$$\text{mol OH}^- = \frac{75}{1000} \times 0.200 = 0.0150 \quad \therefore \text{HA is in XS}$$

	HA	+	OH <sup>-</sup>	→	A <sup>-</sup>	+	H <sub>2</sub> O
before reaction	0.0250		0.0150				
after reaction	0.0100		-		0.0150		

$$\therefore \text{left over [HA]} = \frac{0.0100}{\frac{125}{1000}} = 0.0800$$

$$\therefore \text{formed [A}^-] = \frac{0.0150}{\frac{125}{1000}} = 0.120$$

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

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{10^{-4.76} \times 0.0800}{0.120} = 1.16 \times 10^{-5}$$

$$\text{pH} = -\log(1.16 \times 10^{-5}) = \underline{4.94}$$

### Example – half neutralisation of a weak acid

When half of the HA molecules have reacted with OH<sup>-</sup>, [HA] = [A<sup>-</sup>].  $\therefore K_a = [\text{H}^+]$  or  $\text{pK}_a = \text{pH}$

Calculate the pH of the solution formed when 100 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> ethanoic acid (pK<sub>a</sub> = 4.76) is added to 40 cm<sup>3</sup> of 0.250 mol dm<sup>-3</sup> KOH.

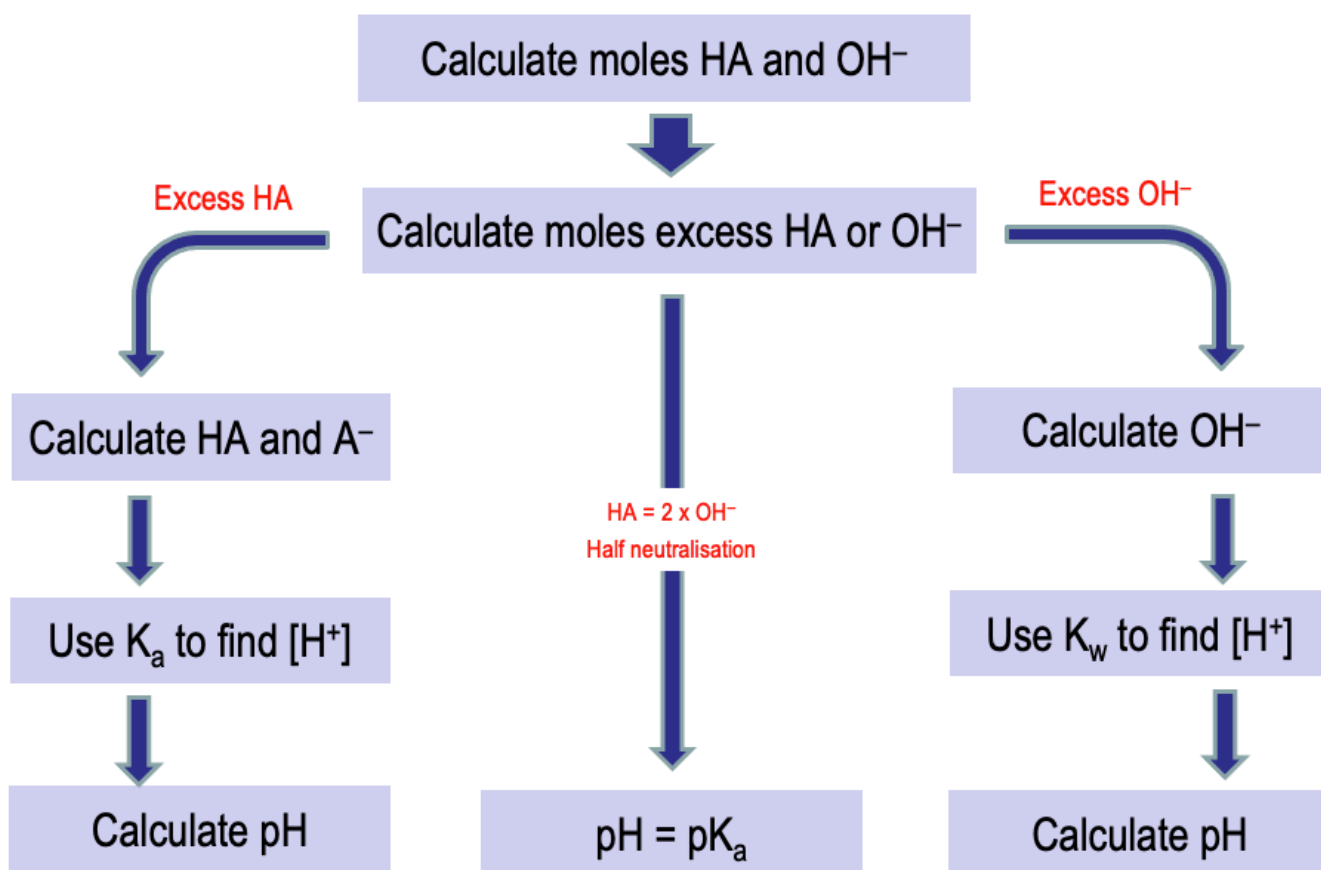
$$\text{mol HA} = \frac{100}{1000} \times 0.200 = 0.0200$$

$$\text{mol OH}^- = \frac{40}{1000} \times 0.250 = 0.0100 \quad \therefore \text{HA is in XS}$$

	HA	+	OH <sup>-</sup>	→	A <sup>-</sup>	+	H <sub>2</sub> O
before reaction	0.0200		0.0100				
after reaction	0.0100		-		0.0100		

half neutralisation and so [HA] = [A<sup>-</sup>]

$$\therefore \text{pH} = \text{pK}_a = \underline{4.76}$$



### TASK 8 – pH of mixtures of weak acids & strong bases

- 1 Calculate the pH of the solution formed when 20 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> methanoic acid (K<sub>a</sub> = 1.7 × 10<sup>-4</sup> mol dm<sup>-3</sup>) is added to 40 cm<sup>3</sup> of 0.080 mol dm<sup>-3</sup> KOH.
- 2 Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> propanoic acid (pK<sub>a</sub> = 4.87) is added to 100 cm<sup>3</sup> of 0.080 mol dm<sup>-3</sup> KOH.
- 3 Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> ethanoic acid (pK<sub>a</sub> = 4.76) is added to 50 cm<sup>3</sup> of 0.250 mol dm<sup>-3</sup> KOH.
- 4 Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> chloroethanoic acid (pK<sub>a</sub> = 2.86) is added to 25 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> Ba(OH)<sub>2</sub>.
- 5 Calculate the pH of the solution formed when 50 cm<sup>3</sup> of 1.50 mol dm<sup>-3</sup> dichloroethanoic acid (K<sub>a</sub> = 0.0513 mol dm<sup>-3</sup>) is added to 100 cm<sup>3</sup> of 2.00 mol dm<sup>-3</sup> KOH.
- 6 Calculate the pH of the solution formed when 25 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> benzenecarboxylic acid (pK<sub>a</sub> = 4.20) is added to 50 cm<sup>3</sup> of 0.0400 mol dm<sup>-3</sup> NaOH.



Finding K<sub>a</sub> for propanoic acid (Chemsheets A2 1082 or 1083)

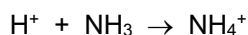
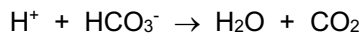
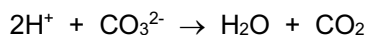
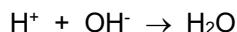


## TASK 9 – A variety of pH calculations so far

- 1 Calculate the pH of  $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .
- 2 Calculate the pH of  $0.250 \text{ mol dm}^{-3}$  methanoic acid ( $K_a = 1.70 \times 10^{-4} \text{ mol dm}^{-3}$ )
- 3 Calculate the pH of  $0.20 \text{ mol dm}^{-3} \text{ Sr(OH)}_2$ .
- 4 Calculate the pH of a mixture of  $20 \text{ cm}^3$  of  $0.500 \text{ mol dm}^{-3} \text{ NaOH}$  and  $80 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3} \text{ HNO}_3$ .
- 5 Calculate the pH of the solution formed when  $100 \text{ cm}^3$  of water is added to  $25 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ NaOH}$ .
- 6 Calculate the pH of a mixture of  $25 \text{ cm}^3$   $0.200 \text{ mol dm}^{-3}$  ethanoic acid ( $\text{p}K_a = 4.76$ ) and  $25 \text{ cm}^3$   $0.100 \text{ mol dm}^{-3} \text{ NaOH}$ .
- 7 Calculate the pH of a mixture of  $100 \text{ cm}^3$   $0.100 \text{ mol dm}^{-3}$  ethanoic acid ( $\text{p}K_a = 4.76$ ) and  $50 \text{ cm}^3$   $0.150 \text{ mol dm}^{-3} \text{ NaOH}$ .
- 8 Calculate the pH of a mixture of  $50 \text{ cm}^3$   $0.200 \text{ mol dm}^{-3}$  propanoic acid ( $\text{p}K_a = 4.87$ ) and  $25 \text{ cm}^3$   $1.00 \text{ mol dm}^{-3} \text{ KOH}$ .

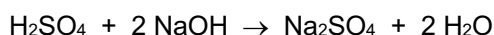
## SECTION 7 – Titration calculations

Remember these ionic equations which help a great deal in titration calculations.



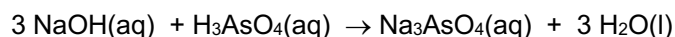
### TASK 10a – Titration calculations

- 1** 25.0 cm<sup>3</sup> of a solution of sodium hydroxide required 18.8 cm<sup>3</sup> of 0.0500 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.



- a) Find the concentration of the sodium hydroxide solution in mol dm<sup>-3</sup>.  
b) Find the concentration of the sodium hydroxide solution in g dm<sup>-3</sup>.

- 2** 25.0 cm<sup>3</sup> of arsenic acid, H<sub>3</sub>AsO<sub>4</sub>, required 37.5 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> sodium hydroxide for neutralisation.



- a) Find the concentration of the acid in mol dm<sup>-3</sup>.  
b) Find the concentration of the acid in g dm<sup>-3</sup>.

- 3** A 250 cm<sup>3</sup> solution of NaOH was prepared. 25.0 cm<sup>3</sup> of this solution required 28.2 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl for neutralisation. Calculate what mass of NaOH was dissolved to make up the original 250 cm<sup>3</sup> solution.

- 4** 3.88 g of a monoprotic acid was dissolved in water and the solution made up to 250 cm<sup>3</sup>. 25.0 cm<sup>3</sup> of this solution was titrated with 0.095 mol dm<sup>-3</sup> NaOH solution, requiring 46.5 cm<sup>3</sup>. Calculate the relative molecular mass of the acid.

- 5** A 1.575 g sample of ethanedioic acid crystals, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.nH<sub>2</sub>O, was dissolved in water and made up to 250 cm<sup>3</sup>. One mole of the acid reacts with two moles of NaOH. In a titration, 25.0 cm<sup>3</sup> of this solution of acid reacted with exactly 15.6 cm<sup>3</sup> of 0.160 mol dm<sup>-3</sup> NaOH. Calculate the value of n.

- 6** A solution of a metal carbonate, M<sub>2</sub>CO<sub>3</sub>, was prepared by dissolving 7.46 g of the anhydrous solid in water to give 1000 cm<sup>3</sup> of solution. 25.0 cm<sup>3</sup> of this solution reacted with 27.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> hydrochloric acid. Calculate the relative formula mass of M<sub>2</sub>CO<sub>3</sub> and hence the relative atomic mass of the metal M.

- 7** A 1.00 g sample of limestone is allowed to react with 100 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> HCl. The excess acid required 24.8 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH solution. Calculate the percentage of calcium carbonate in the limestone.

- 8** An impure sample of barium hydroxide of mass 1.6524 g was allowed to react with 100 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> hydrochloric acid. When the excess acid was titrated against sodium hydroxide, 10.9 cm<sup>3</sup> of sodium hydroxide solution was required. 25.0 cm<sup>3</sup> of the sodium hydroxide required 28.5 cm<sup>3</sup> of the hydrochloric acid in a separate titration. Calculate the percentage purity of the sample of barium hydroxide.

## TASK 10b – Short-cut titration volumes

In each of the following, work out the volume of solution required for neutralisation.

Don't use a calculator, don't work out moles – just use ratios and the fact that one  $\text{H}^+$  reacts with one  $\text{OH}^-/\text{NH}_3$

*For example:*

What volume of  $0.1 \text{ mol dm}^{-3}$  NaOH is needed to neutralise  $50 \text{ cm}^3$  of  $0.2 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$

**NaOH has one  $\text{OH}^-$  per unit;  $\text{H}_2\text{SO}_4$  has two  $\text{H}^+$  ions per unit**

**$\therefore$  reacting ratio is:  $2\text{NaOH} + \text{H}_2\text{SO}_4$**

**$\therefore$  if the solutions had the same concentration, then volume of NaOH would be 2x that of  $\text{H}_2\text{SO}_4$**

**but the  $\text{H}_2\text{SO}_4$  is twice as concentrated as NaOH, so the volume of NaOH would need to be 4x that of the  $\text{H}_2\text{SO}_4$**

**$\therefore$  volume of NaOH =  $4 \times 50 = 200 \text{ cm}^3$**

	Acid	Alkali
1	$25 \text{ cm}^3$ of $1.0 \text{ mol dm}^{-3}$ HCl	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ NaOH
2	$20 \text{ cm}^3$ of $1.0 \text{ mol dm}^{-3}$ $\text{H}_2\text{SO}_4$	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ $\text{NH}_3$
3	$50 \text{ cm}^3$ of $0.5 \text{ mol dm}^{-3}$ HCl	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ $\text{Ba}(\text{OH})_2$
4	$30 \text{ cm}^3$ of $0.2 \text{ mol dm}^{-3}$ $\text{CH}_3\text{COOH}$	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ NaOH
5	..... $\text{cm}^3$ of $2.0 \text{ mol dm}^{-3}$ HCl	$20 \text{ cm}^3$ of $0.5 \text{ mol dm}^{-3}$ NaOH
6	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ $\text{HCOOH}$	$50 \text{ cm}^3$ of $0.1 \text{ mol dm}^{-3}$ NaOH
7	..... $\text{cm}^3$ of $0.2 \text{ mol dm}^{-3}$ HCl	$30 \text{ cm}^3$ of $0.1 \text{ mol dm}^{-3}$ $\text{NH}_3$
8	$25 \text{ cm}^3$ of $0.5 \text{ mol dm}^{-3}$ ethanedioic acid	..... $\text{cm}^3$ of $1.0 \text{ mol dm}^{-3}$ NaOH
9	$100 \text{ cm}^3$ of $0.2 \text{ mol dm}^{-3}$ $\text{H}_2\text{SO}_4$	..... $\text{cm}^3$ of $0.5 \text{ mol dm}^{-3}$ $\text{Ba}(\text{OH})_2$
10	..... $\text{cm}^3$ of $0.02 \text{ mol dm}^{-3}$ $\text{HNO}_3$	$20 \text{ cm}^3$ of $0.05 \text{ mol dm}^{-3}$ $\text{Ca}(\text{OH})_2$

## SECTION 8 – pH curves & indicators

### What are indicators and how do they work?

- Indicators are weak acids where HA and A<sup>-</sup> are different colours.  $HA \rightleftharpoons H^+ + A^-$
- At low pH, HA is the main species present. At high pH, A<sup>-</sup> is the main species present.
- The pH at which the colour changes varies from one indicator to another.
- Note that universal indicator is a mixture of indicators and so shows many colours at different pHs.

indicator	colour of HA	pH range of colour change	colour of A <sup>-</sup>
methyl orange	red	3.2 - 4.4	yellow
phenolphthalein	colourless	8.2 - 10.0	pink

- In a titration, the pH changes rapidly at the end point as the last drop of acid/alkali is added. For an indicator to change colour at this moment where the moles of acid = moles of base, the indicator must change colour within the range of the rapid change in pH at the end point.

### pH curves

- These show how the pH changes as an alkali is added to an acid (or vice versa).
- The equivalence point is when the moles of alkali added equals the moles of acid present – but the pH is not always 7 at the equivalence point.
- In most acid-alkali reactions, the pH curve shows a rapid change in pH around the equivalence point.
- The end point of a titration is when the indicator changes colour, and if a suitable indicator is used then the end point should coincide with the equivalence point.

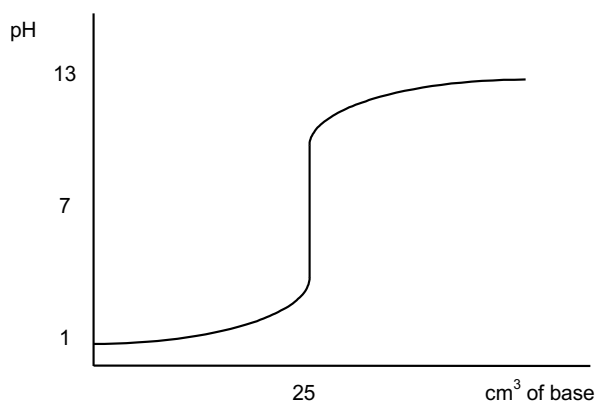


### Plotting pH curves (Chemsheets A2 1086)



The curves below show the pH as  $0.100 \text{ mol dm}^{-3}$  base is added to  $25.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  acid:

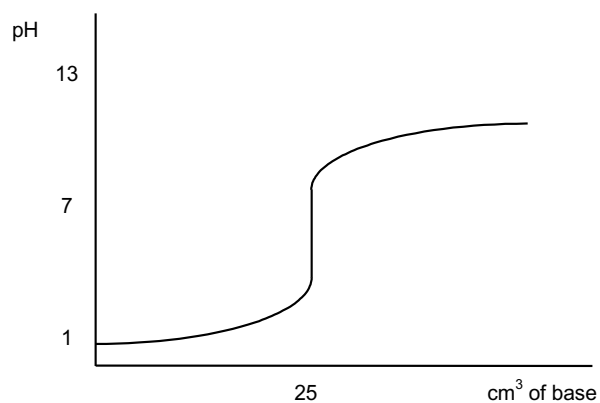
**a) strong acid - strong base**



pH at equivalence:

suitable indicators:

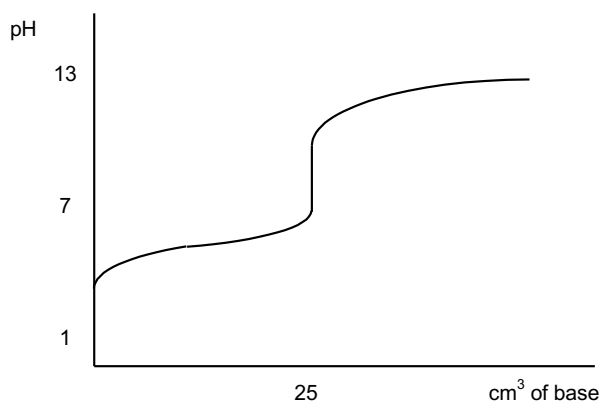
**b) strong acid - weak base**



pH at equivalence:

suitable indicators:

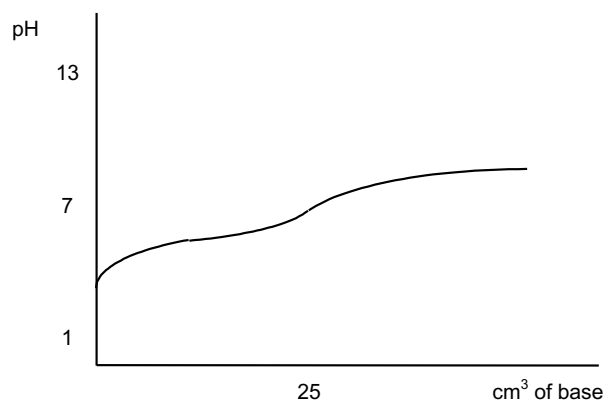
**c) weak acid - strong base**



pH at equivalence:

suitable indicators:

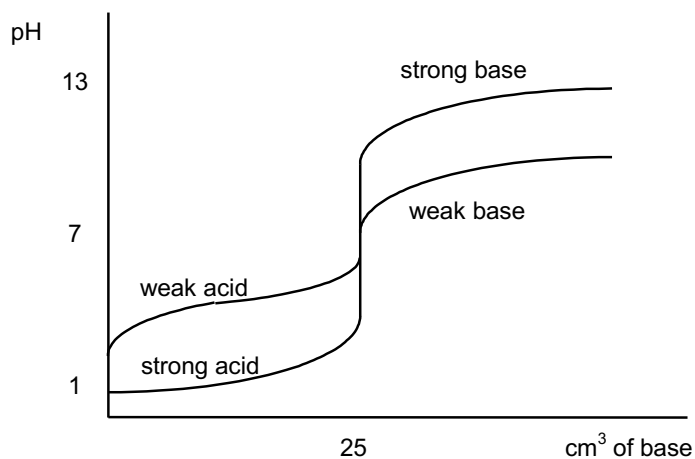
**d) weak acid - weak base**



pH at equivalence:

suitable indicators:

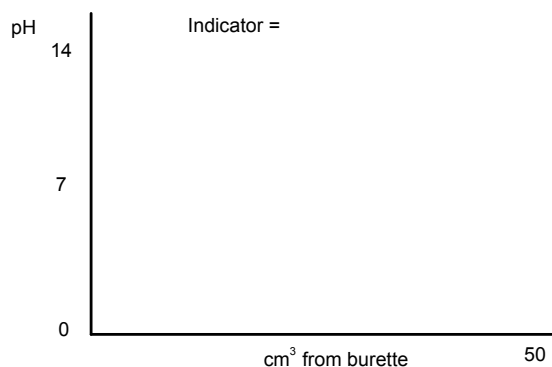
**Summary:**



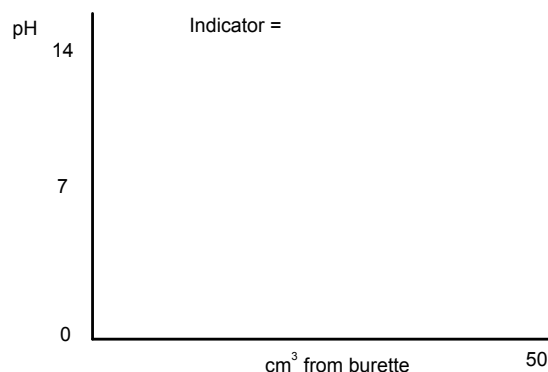
## TASK 11 – Sketching pH curves

Sketch each of the following pH curves on the grids shown, and name a suitable indicator.

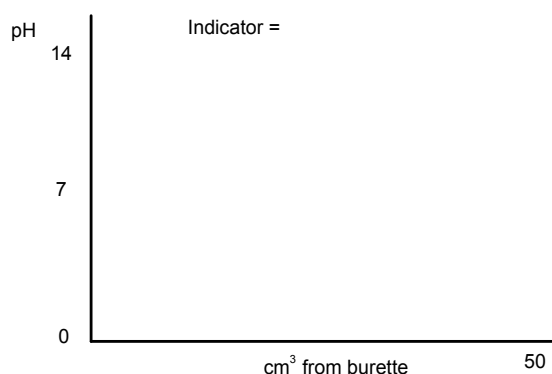
- (1)** Flask 25 cm<sup>3</sup> 0.10 mol dm<sup>-3</sup> HNO<sub>3</sub>  
Burette 50 cm<sup>3</sup> 0.20 mol dm<sup>-3</sup> NaOH



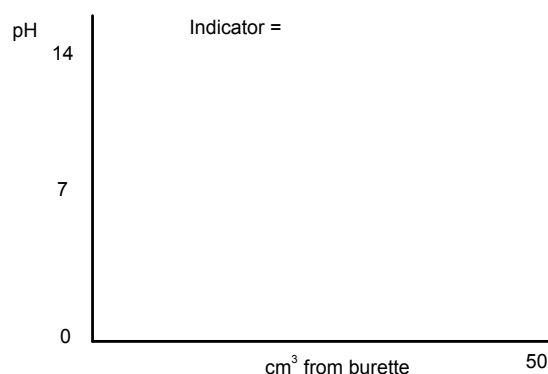
- (2)** Flask 20 cm<sup>3</sup> 0.10 mol dm<sup>-3</sup> NaOH  
Burette 50 cm<sup>3</sup> 0.10 mol dm<sup>-3</sup> HCl



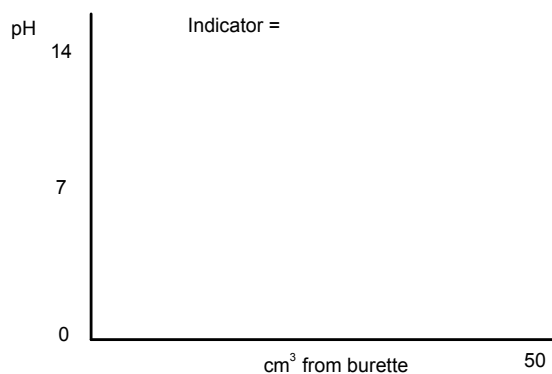
- (3)** Flask 10 cm<sup>3</sup> 0.20 mol dm<sup>-3</sup> HNO<sub>3</sub>  
Burette 50 cm<sup>3</sup> 0.05 mol dm<sup>-3</sup> NaOH



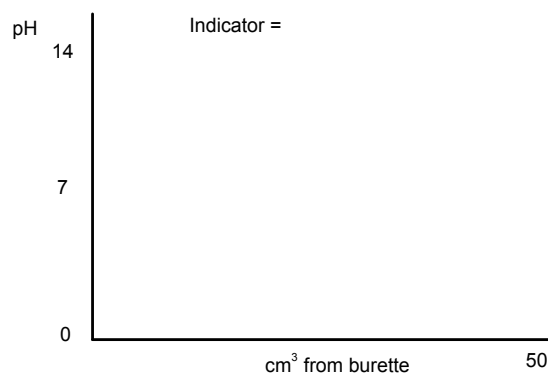
- (4)** Flask 30 cm<sup>3</sup> 1.00 mol dm<sup>-3</sup> NH<sub>3</sub>  
Burette 50 cm<sup>3</sup> 1.00 mol dm<sup>-3</sup> HCl



- (5)** Flask 20 cm<sup>3</sup> 0.20 mol dm<sup>-3</sup> CH<sub>3</sub>COOH  
Burette 50 cm<sup>3</sup> 0.05 mol dm<sup>-3</sup> NaOH



- (6)** Flask 50 cm<sup>3</sup> 0.500 mol dm<sup>-3</sup> NH<sub>3</sub>  
Burette 50 cm<sup>3</sup> 1.00 mol dm<sup>-3</sup> methanoic acid



## SECTION 9 – Buffer solutions

### What is a buffer solution?

- Buffer solution = solution that resists changes in pH when small amounts of acid or alkali are added.
- Note – the pH does change, just not by much!
- Acidic buffer solutions have a pH lower than 7.
- Basic buffer solutions have a pH higher than 7.

### Examples of buffer solutions

#### **Acidic buffers**

- Acidic buffer solutions are made from a mixture of a weak acid and one of its salts (i.e. HA and A<sup>-</sup>) (e.g. ethanoic acid & sodium ethanoate).
- An acidic buffer solution can also be made by mixing an excess of a weak acid with a strong alkali as it results in a mixture of HA and A<sup>-</sup>.
- The key in an acidic buffer solution is that the [acid] and [salt] are much higher than [H<sup>+</sup>].

#### **Basic buffers**

- Basic buffer solutions are made from a mixture of a weak alkali and one of its salts (e.g. ammonia & ammonium chloride).
- A basic buffer solution can also be made by mixing an excess of a weak alkali with a strong acid
- The key in a basic buffer solution is that the [base] and [salt] are much higher than [OH<sup>-</sup>].

Type of buffer	Acidic buffer		Basic buffer	
Components	Weak acid + one of its salts [acid] & [salt] >> [H <sup>+</sup> ]		Weak base + one of its salts [base] & [salt] >> [OH <sup>-</sup> ]	
Route 1	Mixture of weak acid and one of its salts	<i>e.g. ethanoic acid + sodium ethanoate</i>	Mixture of weak base and one of its salts	<i>e.g. ammonia + ammonium chloride</i>
Route 2	Mixture of an excess of weak acid and a strong base	<i>e.g. <b>excess</b> ethanoic acid + sodium hydroxide</i>	Mixture of an excess of weak base and a strong acid	<i>e.g. <b>excess</b> ammonia + hydrochloric acid</i>

## How do buffer solutions work?

- The pH of an acidic buffer solution is found using the  $K_a$  expression:

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

- Therefore the pH of an acidic buffer depends on the ratio of [HA] to [A<sup>-</sup>] (i.e. the ratio of [acid] to [salt]).
- In a similar way, the pH of a basic buffer depends on the ratio of [base] to [salt]
- When small amounts of acid or alkali are added, the ratio remains roughly constant and so the pH hardly changes. If large amounts of acid or alkali are added, the ratio would change significantly and so the pH would change significantly.

	Acidic buffer (e.g. CH <sub>3</sub> COOH + CH <sub>3</sub> COO <sup>-</sup> )	Basic buffer (e.g. NH <sub>3</sub> , NH <sub>4</sub> <sup>+</sup> )
<b>Add a little H<sup>+</sup></b>	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ <p>The added H<sup>+</sup> is removed by reaction with CH<sub>3</sub>COO<sup>-</sup> to form CH<sub>3</sub>COOH.</p> <p>The [CH<sub>3</sub>COO<sup>-</sup>] falls slightly and the [CH<sub>3</sub>COOH] rises slightly, but as [CH<sub>3</sub>COOH] &amp; [CH<sub>3</sub>COO<sup>-</sup>] &gt;&gt; [H<sup>+</sup>], the ratio of [CH<sub>3</sub>COOH]/[CH<sub>3</sub>COO<sup>-</sup>] remains roughly constant.</p>	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ <p>The added H<sup>+</sup> is removed by reaction with OH<sup>-</sup>, so some NH<sub>3</sub> reacts to replace the OH<sup>-</sup>.</p> <p>The [NH<sub>3</sub>] falls slightly and the [NH<sub>4</sub><sup>+</sup>] rises slightly, but as [NH<sub>3</sub>] &amp; [NH<sub>4</sub><sup>+</sup>] &gt;&gt; [OH<sup>-</sup>], the ratio of [NH<sub>3</sub>]/[NH<sub>4</sub><sup>+</sup>] remains roughly constant.</p>
<b>Add a little OH<sup>-</sup></b>	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ <p>The added OH<sup>-</sup> reacts with H<sup>+</sup>, and so some CH<sub>3</sub>COOH breaks down to replace that H<sup>+</sup>.</p> <p>The [CH<sub>3</sub>COO<sup>-</sup>] rises slightly and the [CH<sub>3</sub>COOH] falls slightly, but as [CH<sub>3</sub>COOH] &amp; [CH<sub>3</sub>COO<sup>-</sup>] &gt;&gt; [H<sup>+</sup>], the ratio of [CH<sub>3</sub>COOH]/[CH<sub>3</sub>COO<sup>-</sup>] remains roughly constant.</p>	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ <p>The added OH<sup>-</sup> is removed by reaction with NH<sub>4</sub><sup>+</sup> to form NH<sub>3</sub>.</p> <p>The [NH<sub>3</sub>] rises slightly and the [NH<sub>4</sub><sup>+</sup>] falls slightly, but as [NH<sub>3</sub>] &amp; [NH<sub>4</sub><sup>+</sup>] &gt;&gt; [OH<sup>-</sup>], the ratio of [NH<sub>3</sub>]/[NH<sub>4</sub><sup>+</sup>] remains roughly constant.</p>
<b>Add water</b>	The ratio of [CH <sub>3</sub> COOH] to [CH <sub>3</sub> COO <sup>-</sup> ] remains constant and so the pH remains constant.	The ratio of [NH <sub>3</sub> ] to [NH <sub>4</sub> <sup>+</sup> ] remains constant and so the pH remains constant.



### Making a buffer solution (Chemsheets A2 1089)



### Calculating the pH of acidic buffers

- 1) A buffer solution was made by adding 2.05 g of sodium ethanoate to 0.500 dm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> ethanoic acid. Calculate the pH of this solution ( $K_a$  for ethanoic acid =  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup>).

$$M_r \text{CH}_3\text{COONa} = 82.0$$

$$\text{mol CH}_3\text{COONa} = 2.05 / 82.0 = 0.0250$$

$$\text{mol CH}_3\text{COO}^- = 0.0250$$

$$[\text{A}^-] = \frac{0.0250}{0.500} = 0.0500$$

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

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{1.74 \times 10^{-5} \times 0.01}{0.050} = 3.48 \times 10^{-6}$$

$$\text{pH} = -\log (3.48 \times 10^{-6}) = \underline{5.46}$$

- 2) a) A buffer solution was made by mixing 25.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> ethanoic acid with 25 cm<sup>3</sup> of 0.400 mol dm<sup>-3</sup> sodium hydroxide. Find the pH of this buffer. ( $K_a$  for ethanoic acid =  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup>).

$$\text{mol HA} = \frac{25}{1000} \times 1.00 = 0.0250$$

$$\text{mol OH}^- = \frac{25}{1000} \times 0.400 = 0.0100 \quad \therefore \text{HA is in XS}$$

	HA	+	OH <sup>-</sup>	→	A <sup>-</sup>	+	H <sub>2</sub> O
before reaction	0.0250		0.0100				
after reaction	0.0150		-		0.0100		

$$\therefore \text{left over } [\text{HA}] = \frac{0.0150}{50/1000}$$

$$\therefore \text{formed } [\text{A}^-] = \frac{0.0100}{50/1000}$$

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

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{1.74 \times 10^{-5} \times \frac{0.0150}{50/1000}}{\frac{0.0100}{50/1000}} = 2.61 \times 10^{-5}$$

$$\text{pH} = -\log (2.61 \times 10^{-5}) = \underline{4.58}$$

- b) Calculate the new pH of the buffer if 0.2 cm<sup>3</sup> of 0.50 mol dm<sup>-3</sup> sulfuric acid is added to the sample from part (a).

$$\text{mol H}^+ \text{ added} = 2 \times 0.2/1000 \times 0.50 = 0.0002$$

	$\text{A}^- + \text{H}^+ \rightarrow \text{HA}$		
before reaction	0.0100	0.0002	0.0150
after reaction	0.0098		0.0152

$$\therefore [\text{HA}] = \frac{0.0152}{50.2/1000}$$

$$\therefore [\text{A}^-] = \frac{0.0098}{50.2/1000}$$

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

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{1.74 \times 10^{-5} \times \frac{0.0152}{50.2/1000}}{\frac{0.0098}{50.2/1000}} = 2.70 \times 10^{-5}$$

$$\text{pH} = -\log (2.70 \times 10^{-5}) = 4.57$$

- c) Calculate the new pH of the buffer if 1.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> sodium hydroxide is added to the sample from part (a).

$$\text{mol OH}^- \text{ added} = 1.0/1000 \times 0.100 = 0.0001$$

	$\text{HA}$	+	$\text{OH}^-$	$\rightarrow$	$\text{A}^-$	+	$\text{H}_2\text{O}$
before reaction	0.0150		0.0001		0.0100		
after reaction	0.0149		-		0.0101		

$$\therefore [\text{HA}] = \frac{0.0149}{51.0/1000}$$

$$\therefore [\text{A}^-] = \frac{0.0101}{51.0/1000}$$

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

$$[\text{H}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]} = \frac{1.74 \times 10^{-5} \times \frac{0.0149}{51.0/1000}}{\frac{0.0101}{51.0/1000}} = 2.57 \times 10^{-5}$$

$$\text{pH} = -\log (2.57 \times 10^{-5}) = 4.59$$

## TASK 12 – Buffer solution calculations

- 1** Calculate the pH of the following buffer solutions made by mixing weak acids with their salts.
- 50.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> methanoic acid ( $K_a = 1.78 \times 10^{-4}$  mol dm<sup>-3</sup>) mixed with 20.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> sodium methanoate.
  - 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> butanoic acid ( $pK_a = 4.82$ ) mixed with 20.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> sodium butanoate.
  - 1.00 g of potassium ethanoate is dissolved in 50.0 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> ethanoic acid ( $K_a = 1.74 \times 10^{-5}$  mol dm<sup>-3</sup>).
- 2** Calculate the pH of the following buffer solutions made by mixing an excess of weak acids with strong bases.
- 25.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> methanoic acid ( $K_a = 1.78 \times 10^{-4}$  mol dm<sup>-3</sup>) is mixed with 10.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> sodium hydroxide.
  - 100 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> ethanoic acid ( $K_a = 1.78 \times 10^{-4}$  mol dm<sup>-3</sup>) is mixed with 50.0 cm<sup>3</sup> of 0.800 mol dm<sup>-3</sup> sodium hydroxide.
- 3**
- Calculate the pH of a buffer solution formed by mixing 20.0 cm<sup>3</sup> of 1.20 mol dm<sup>-3</sup> methanoic acid ( $K_a = 1.78 \times 10^{-4}$  mol dm<sup>-3</sup>) with 20.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> sodium methanoate.
  - Calculate the pH of this buffer solution if 1.2 cm<sup>3</sup> of 0.40 mol dm<sup>-3</sup> sodium hydroxide is added.
- 4**
- Calculate the pH of a buffer solution formed by mixing 50.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> ethanoic acid ( $K_a = 1.74 \times 10^{-5}$  mol dm<sup>-3</sup>) with 10.0 cm<sup>3</sup> of 0.800 mol dm<sup>-3</sup> sodium hydroxide.
  - Calculate the pH of this buffer solution if 2.0 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> hydrochloric acid is added.
- 5**
- What mass of sodium methanoate should be dissolved in 250 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> methanoic acid to form a buffer solution with a pH of 5.20 ( $K_a$  for methanoic acid =  $1.78 \times 10^{-4}$  mol dm<sup>-3</sup>).
  - What mass of sodium ethanoate should be dissolved in 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> ethanoic acid to form a buffer solution with a pH of 3.50 ( $K_a$  for ethanoic acid =  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup>).
- 6**
- 2.00 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH is added to 100.0 cm<sup>3</sup> of water. Calculate the **change** in pH of the water.
  - 2.00 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaOH is added to 100 cm<sup>3</sup> of a buffer solution containing 0.150 mol dm<sup>-3</sup> ethanoic acid and 0.100 mol dm<sup>-3</sup> sodium ethanoate ( $K_a$  ethanoic acid =  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup>). Calculate the **change** in pH of the buffer solution.
  - Explain why the pH of the buffer solution only changes slightly compared to water.

### TASK 13 – One final lovely mixture of calculations just for fun

- 1** Calculate the pH of  $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .
- 2** Calculate the pH of the solution formed when  $200 \text{ cm}^3$  of water are added to  $50 \text{ cm}^3$  of  $0.500 \text{ mol dm}^{-3} \text{ HCl}$ .
- 3** Calculate the pH of  $0.500 \text{ mol dm}^{-3} \text{ NaOH}$  ( $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ).
- 4** Calculate the pH change when water is added to  $25 \text{ cm}^3$  of  $0.250 \text{ mol dm}^{-3} \text{ NaOH}$  to prepare  $1.00 \text{ dm}^3$  of solution ( $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ).
- 5** Calculate the pH of  $0.100 \text{ mol dm}^{-3}$  chloroethanoic acid given that  $K_a = 1.38 \times 10^{-3} \text{ mol dm}^{-3}$ .
- 6** Find the pH of  $0.100 \text{ mol dm}^{-3}$  benzenecarboxylic acid ( $K_a = 6.31 \times 10^{-5} \text{ mol dm}^{-3}$ ) when it has been half neutralised by NaOH.
- 7** Calculate the pH of water at  $50^\circ\text{C}$  given that  $K_w = 5.476 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at  $50^\circ\text{C}$  and state and explain whether the water is still neutral.
- 8** Find the pH of the buffer solution prepared by adding  $1.00 \text{ g}$  of sodium ethanoate to  $250 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  ethanoic acid ( $K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$ ).
- 9** Calculate the pH of the solution formed when  $25 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ NaOH}$  is added to  $50 \text{ cm}^3$  of  $0.250 \text{ mol dm}^{-3} \text{ HNO}_3$ .
- 10** Calculate the pH of the solution formed when  $100 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ NaOH}$  is added to  $20 \text{ cm}^3$  of  $0.150 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ .
- 11** Calculate the pH of the solution formed when  $50 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ NaOH}$  is added to  $100 \text{ cm}^3$  of  $0.300 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$  ( $K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$ ).
- 12** Calculate the pH of the solution formed when  $50 \text{ cm}^3$  of  $0.0500 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$  is added to  $20 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ HCOOH}$  ( $K_a = 1.78 \times 10^{-4} \text{ mol dm}^{-3}$ ).



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### TASK 1 – Bronsted-Lowry acids & bases

- |   |   |   |  |   |  |
|---|---|---|--|---|--|
| 1 | Acid = $\text{H}_2\text{O}$ , base = $\text{NH}_3$    | 2 | Acid = $\text{HCl}$ , base = $\text{H}_2\text{O}$      | 3 | Acid = $\text{HCOOH}$ , base = $\text{KOH}$    |
| 4 | Acid = $\text{HCl}$ , base = $\text{CH}_3\text{COOH}$ | 5 | Acid = $\text{HCl}$ , base = $\text{NH}_3$             | 6 | Acid = $\text{HCO}_3^-$ , base = $\text{OH}^-$ |
| 7 | Acid = $\text{H}^+$ , base = $\text{HCO}_3^-$         | 8 | Acid = $\text{H}_2\text{SO}_4$ , base = $\text{HNO}_3$ |   |  |

### TASK 2 – pH of strong acids

- |   |   |                       |   |        |   |        |   |                            |
|---|---|-----------------------|---|--------|---|--------|---|----------------------------|
| 1 | a | 0.70                  | b | 1.30   | c | 1.10   | d | -0.30                      |
| 2 | a | $2.82 \times 10^{-4}$ | b | 0.0100 | c | 0.0501 | d | $1.58 \text{ mol dm}^{-3}$ |
| 3 | a | 1.48                  | b | 0.80   | c | 0.10   | d | 0.82                       |
| 4 | a | 0.56                  | b | 0.39   | c | 0.10   | d | -0.31                      |

### TASK 3 – pH of strong bases

- |   |   |       |   |        |   |                             |
|---|---|-------|---|--------|---|-----------------------------|
| 1 | a | 13.18 | b | 12.70  | c | 13.60                       |
| 2 | a | 2.00  | b | 0.0158 | c | $0.501 \text{ mol dm}^{-3}$ |
| 3 | a | 12.30 | b | 13.20  | c | 13.00                       |
| 4 | a | 13.70 | b | 14.25  | c | 12.22                       |

### TASK 4 – pH of mixtures of strong acids and strong bases

- |   |                                 |   |      |   |                                  |   |       |   |      |
|---|---------------------------------|---|------|---|----------------------------------|---|-------|---|------|
| 1 | 2.00                            | 2 | 1.48 | 3 | 13.12                            | 4 | 13.15 | 5 | 1.60 |
| 6 | new pH = 1.00, increase by 0.30 |   |      | 7 | new pH = 1.60, decrease by 11.58 |   |       |   |      |

### TASK 5 – A variety of pH calculations so far

- 1 a 13.48      b 0.70      c -0.48      d 12.70  
2 a 6.63      b still neutral as  $[H^+] = [OH^-]$   
3 a 0.40      b 12.00  
4 a 12.52      b 0.93  
5 13.74

### TASK 6 – The pH of weak acids

- 1 a 2.51      b 2.76      c 1.87  
2 a  $5.01 \times 10^{-5}$       b  $5.50 \times 10^{-3} \text{ mol dm}^{-3}$   
3 a ethanoic acid      b propenoic acid  
4  $4.79 \times 10^{-5} \text{ mol dm}^{-3}$

### TASK 7 – Reactions of weak acids

- 1)  $HA = 1.5, OH^- = 0, A^- = 2.5$   
2)  $HA = 3.4, OH^- = 0, A^- = 2.6$   
3)  $HA = 0, OH^- = 0.10, A^- = 0.15$   
4)  $HA = 0.15, OH^- = 0, A^- = 0.15$   
5)  $HA = 0.0075, OH^- = 0, A^- = 0.0025$   
6)  $HA = 0, OH^- = 0.0275, A^- = 0.0125$   
7)  $HA = 0.0002, OH^- = 0, A^- = 0.0008$

### TASK 8 – pH of mixtures of weak acids & strong bases

- 1 12.30      2 4.54      3 4.76      4 2.26      5 13.92      6 3.14

### TASK 9 – A variety of pH calculations so far

- 1 0.70      2 2.19      3 13.60      4 1.22      5 12.30  
6 4.76      7 5.24      8 13.30

### TASK 10a – Titration calculations

- |   |        |                             |      |                         |   |   |   |                 |
|---|--------|-----------------------------|------|-------------------------|---|---|---|-----------------|
| 1 | a      | 0.0752 mol dm <sup>-3</sup> | b    | 3.01 g dm <sup>-3</sup> |   |   |   |                 |
| 2 | a      | 0.050 mol dm <sup>-3</sup>  | b    | 7.10 g dm <sup>-3</sup> |   |   |   |                 |
| 3 | 1.13 g | 4                           | 87.8 | 5                       | 2 | 6 | K | 7 87.7% 8 90.8% |

### TASK 10b – Short-cut titration calculations

- |   |                    |   |                    |   |                    |    |                     |   |                   |   |                    |
|---|--------------------|---|--------------------|---|--------------------|----|---------------------|---|-------------------|---|--------------------|
| 1 | 50 cm <sup>3</sup> | 2 | 80 cm <sup>3</sup> | 3 | 25 cm <sup>3</sup> | 4  | 12 cm <sup>3</sup>  | 5 | 5 cm <sup>3</sup> | 6 | 10 cm <sup>3</sup> |
| 7 | 15 cm <sup>3</sup> | 8 | 25 cm <sup>3</sup> | 9 | 40 cm <sup>3</sup> | 10 | 100 cm <sup>3</sup> |   |                   |   |                    |

### TASK 12 – Buffer solution calculations

- |   |   |                           |   |                          |   |      |
|---|---|---------------------------|---|--------------------------|---|------|
| 1 | a | 3.35                      | b | 4.72                     | c | 4.77 |
| 2 | a | 4.35                      | b | 3.57                     |   |      |
| 3 | a | 3.37                      | b | 3.40                     |   |      |
| 4 | a | 4.43                      | b | 4.40                     |   |      |
| 5 | a | 47.9 g                    | b | 0.0113 g                 |   |      |
| 6 | a | pH = 11.29, change = 4.29 | b | pH = 4.60, change = 0.02 |   |      |

### TASK 13 – One final lovely mixture of calculations just for fun

- |    |   |   |      |   |       |    |       |    |      |   |      |
|----|---|---|------|---|-------|----|-------|----|------|---|------|
| 1  | 0.70  | 2 | 1.00 | 3 | 13.70 | 4  | 1.60  | 5  | 1.93 | 6 | 4.20 |
| 7  | 6.63, neutral as [H <sup>+</sup> ] = [OH <sup>-</sup> ] | 8 | 4.45 | 9 | 0.88  | 10 | 12.52 | 11 | 4.06 |   |      |
| 12 | 12.63   |   |      |   |       |    |       |    |      |   |      |