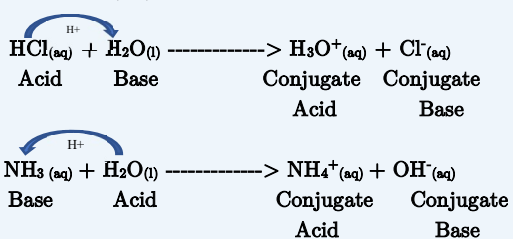


**The Basics**

**Bronsted Lowry Acid:** Proton (H<sup>+</sup>) Donor

**Bronsted Lowry Base:** Proton (H<sup>+</sup>) Acceptor



Water shows Amphoteric behaviour as it can behave as an acid or base as shown above. Another e.g. is HNO<sub>3</sub>, when creating the NO<sub>2</sub><sup>+</sup> electrophile in the nitration of Benzene.

**Calculating pH:**

The below formula can be used to calculate the pH of a solution, given the [H<sup>+</sup>]:

$$pH = -\log[H^+]$$

where [H<sup>+</sup>] is the concentration of hydrogen ions (mol/dm<sup>3</sup>)

The above can be rearranged to calculate [H<sup>+</sup>] as follows:

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

**E.g. 1**

Calculate the pH of a 0.12mol/dm<sup>3</sup> [H<sup>+</sup>] solution?

$$pH = -\log(0.12)$$

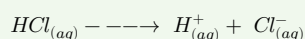
$$pH = 0.92$$

**Calculating pH of Strong Acids**

**Strong Acid:** defined as one that **fully dissociates**.

**E.g.2**

Calculate the pH of a 0.12 mol/dm<sup>3</sup> HCl solution?



$$pH = -\log[H^+]$$

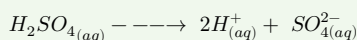
$$pH = -\log(0.12)$$

$$pH = 0.92$$

Note: HCl is a monoprotic acid, as one mole of HCl releases one proton (H<sup>+</sup>) upon dissociation.

**E.g.3**

Calculate the pH of a 0.12 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solution?



$$pH = -\log[H^+]$$

$$pH = -\log(0.24)$$

$$pH = 0.63$$

Note: H<sub>2</sub>SO<sub>4</sub> is a diprotic acid, as one mole of the acid releases 2 protons (H<sup>+</sup>) upon dissociation.

**E.g.4**

Calculate the concentration of a pH=0.92 HCl (aq)?

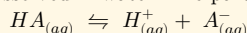
$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-0.92}$$

$$[H^+] = 0.12 \text{ mol/dm}^3$$

**Calculating pH of Weak Acids**

**Weak Acid:** defined as one that only **partially dissociates** when dissolved in water. The partial dissociation can be represented by the equilibrium as follows:



Since, weak acids do not dissociate completely, the acid dissociation constant represents the dissociation as follows:

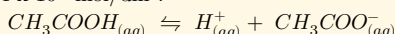
$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} = \frac{[Products]}{[Reactants]}$$

To calculate the pH of a weak acid, the above equation can be simplified to the below based on the assumptions:

$$K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]}$$

**E.g. 5**

Calculate the pH of a 0.12mol/dm<sup>3</sup> ethanoic acid? K<sub>a</sub>= 1.74 x 10<sup>-5</sup> mol/dm<sup>3</sup>?



$$K_a = \frac{[H^+_{(aq)}][CH_3COO^-_{(aq)}]}{[CH_3COOH_{(aq)}]} \quad \text{simplified to} \quad K_a = \frac{[H^+_{(aq)}]^2}{[CH_3COOH_{(aq)}]}$$

$$[H^+]^2_{(aq)} = K_a \times [CH_3COOH_{(aq)}]$$

$$[H^+]_{(aq)} = \sqrt{K_a \times [CH_3COOH_{(aq)}]} = \sqrt{1.74 \times 10^{-5} \times 0.12} = 1.445 \times 10^{-3} \text{ mol/dm}^3$$

$$pH = -\log[H^+]_{(aq)} = -\log(1.445 \times 10^{-3}) = 2.84$$

**Assumptions:**

- 1) [H<sup>+</sup>]<sub>eqm</sub> = [A<sup>-</sup>]<sub>eqm</sub>, since acid releases in 1:1 ratio.
- 2) [HA]<sub>eqm</sub> = [HA]<sub>initial</sub>, dissociation is small, hence difference between initial and eqm concentrations is negligible.

**Ionic Product of Water**

Water dissociates as follows: H<sub>2</sub>O<sub>aq</sub> ⇌ H<sup>+</sup><sub>aq</sub> + OH<sup>-</sup><sub>aq</sub>, which gives rise to the below expression:

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

K<sub>w</sub> can be used for two purposes:

- 1) Calculate the pH of pure water. In water [H<sup>+</sup>]=[OH<sup>-</sup>].
- 2) Calculate the pH of strong bases (as equation consists OH<sup>-</sup> concentration).

Note: K<sub>w</sub> is known as the ionic dissociation constant of water. At 25°C, K<sub>w</sub> is **1x10<sup>-14</sup>mol<sup>2</sup>dm<sup>-6</sup>**. As temperature increases, the value of K<sub>w</sub> increases, as the dissociation of water is endothermic. i.e. increase temp, eqm shifts to the right.

**E.g.6**

Calculate pH of pure water at 25°C?

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

$$K_w = [H^+]^2$$

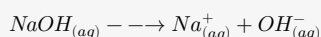
$$1 \times 10^{-14} = [H^+]^2$$

$$[H^+] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ mol/dm}^3$$

$$pH = -\log[H^+] = -\log(1 \times 10^{-7}) = 7$$

**E.g.7**

Calculate pH of 0.12 mol/dm<sup>3</sup> NaOH(aq)?



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

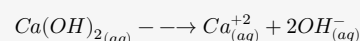
$$1 \times 10^{-14} = [H^+][0.12]$$

$$[H^+] = 8.33 \times 10^{-14}$$

$$pH = -\log(8.33 \times 10^{-14}) = 13.08$$

**E.g.8**

Calculate pH of 0.12 mol/dm<sup>3</sup> Ca(OH)<sub>2</sub>(aq)?



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

$$1 \times 10^{-14} = [H^+][0.24]$$

$$[H^+] = 4.16 \times 10^{-14}$$

$$pH = -\log(4.16 \times 10^{-14}) = 13.38$$

### Calculating pH of acid base reactions

Above we looked at calculating the pH of both acids and bases. In an acid base type reaction, we may have excess acid or base remaining if more acid or base has been added past the neutralisation point. This excess acid or base can result in an acidic or basic solution. Let's look at a few examples:

Steps:

- 1) Write equation for the neutralisation reaction
- 2) Calculate moles of acid and base
- 3) Calculate moles of excess species
- 4) Calculate new concentration, then follow pH calculation as above depending on type of Acid/Base.

#### E.g.9

30cm<sup>3</sup> of 0.6mol/dm<sup>3</sup> Hydrochloric acid is added to 50cm<sup>3</sup> of 0.2mol/dm<sup>3</sup> Sodium Hydroxide. Calculate the pH of the final solution:



$$\text{moles of } HCl = \frac{C \times V}{1000} = \frac{30 \times 0.6}{1000} = 0.018 \text{ moles}$$
$$\therefore \text{moles of } H^+ = 0.018 \text{ moles}$$

$$\text{moles of } NaOH = \frac{C \times V}{1000} = \frac{50 \times 0.2}{1000} = 0.010 \text{ moles}$$
$$\therefore \text{moles of } OH^- = 0.010 \text{ moles}$$

$$\text{moles of excess } H^+_{(aq)} = 0.018 - 0.010 = 0.008 \text{ moles}$$

Now that we have the excess moles of H<sup>+</sup>, we require the concentration of H<sup>+</sup>, so that we can calculate pH:

$$N = 0.008 \text{ moles}$$

$$V = 80 \text{ cm}^3$$

$$C = \frac{0.008 \times 1000}{80} = 0.1 \text{ mol/dm}^3$$

$$pH = -\log[H^+] = -\log(0.1) = 1$$

#### E.g.10

30cm<sup>3</sup> of 0.6mol/dm<sup>3</sup> Sulphuric acid is added to 40cm<sup>3</sup> of 0.8mol/dm<sup>3</sup> Potassium Hydroxide. Calculate the pH of the final solution:



$$\text{moles of } H_2SO_4 = \frac{30 \times 0.6}{1000} = 0.018 \text{ moles}$$
$$\therefore \text{moles of } H^+ = 0.036 \text{ moles}$$

$$\text{moles of } KOH = \frac{C \times V}{1000} = \frac{40 \times 0.8}{1000} = 0.032 \text{ moles}$$
$$\therefore \text{moles of } OH^- = 0.032 \text{ moles}$$

$$\text{moles of excess } H^+_{(aq)} = 0.036 - 0.032 = 0.004 \text{ moles}$$

Now that we have the excess moles of H<sup>+</sup>, we require the concentration of H<sup>+</sup>, so that we can calculate pH:

$$N = 0.004 \text{ moles}$$

$$V = 70 \text{ cm}^3$$

$$C = \frac{0.004 \times 1000}{70} = 0.057 \text{ mol/dm}^3$$

$$pH = -\log[H^+] = -\log(0.057) = 1.24$$

#### E.g.11

In the above examples, the strong acid was in excess, hence we were able to apply the pH equation right away. If the strong base was in excess, we would have to use K<sub>w</sub> as discussed in the strong base section.

30cm<sup>3</sup> of 0.6mol/dm<sup>3</sup> Nitric acid is added to 20cm<sup>3</sup> of 0.8mol/dm<sup>3</sup> Calcium Hydroxide. Calculate the pH of the final solution:



$$\text{moles of } HNO_3 = \frac{C \times V}{1000} = \frac{30 \times 0.6}{1000} = 0.018 \text{ moles} \quad \therefore \text{moles of } H^+ = 0.018 \text{ moles}$$

$$\text{moles of } Ca(OH)_2 = \frac{C \times V}{1000} = \frac{20 \times 0.8}{1000} = 0.016 \text{ moles} \quad \therefore \text{moles of } OH^- = 0.032 \text{ moles}$$

$$\text{moles of excess } OH^-_{(aq)} = 0.032 - 0.018 = 0.014 \text{ moles}$$

Now that we have the excess moles of OH<sup>-</sup>, we require the concentration of OH<sup>-</sup>, so that we can calculate pH:

$$n = 0.014 \text{ moles}$$

$$V = 50 \text{ cm}^3$$

$$[OH^-] = \frac{0.014 \times 1000}{50} = 0.28 \text{ mol/dm}^3$$

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

$$1 \times 10^{-14} = [H^+] \times 0.28$$

$$[H^+] = \frac{1 \times 10^{-14}}{0.28} = 3.57 \times 10^{-14} \text{ mol/dm}^3$$

$$pH = -\log[H^+] = -\log(3.57 \times 10^{-14}) = 13.45$$

### Buffers

A **buffer solution** is one which can resist a change in pH upon addition of small amounts of acid or alkali.

#### Acidic Buffer:

is one that consists of a weak acid and its conjugate base:

a) CH<sub>3</sub>COOH & CH<sub>3</sub>COO<sup>-</sup>

b) CH<sub>3</sub>CH<sub>2</sub>COOH & CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup>

#### Basic Buffer:

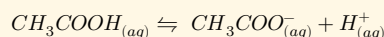
is one that consists of a weak base and its conjugate acid (salt). E.g. include:

a) NH<sub>3</sub> & NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>

b) CH<sub>3</sub>NH<sub>2</sub> & CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>

### How an Acidic Buffer works:

As mentioned above, an acidic buffer consists of a **weak acid** and **its conjugate base**. A buffer solution consisting of ethanoic acid (weak acid) and ethanoate (conjugate base), can be represented below:



Upon addition of small amounts of Acid ( $H^+$ ):

- Adding an acid ( $H^+$ ) is equivalent to increasing  $H^+$  concentration. Hence, system will reduce this by added  $H^+$  reacting with  $CH_3COO^-$ .
- This causes eqm to shift to the left.
- Ratio of Acid/Salt remains relatively constant hence pH remains fairly unchanged.

Upon addition of small amounts of Alkali ( $OH^-$ ):

- Adding an alkali ( $OH^-$ ) will react with  $H^+$  to form  $H_2O$ .
- The above reaction causes the  $H^+$  concentration to decrease. Hence, above eqm shifts to the right to replace  $H^+$  ions.
- Ratio of Acid/Salt remains relatively constant hence pH remains fairly unchanged.

### Making an acidic buffer

Recall that an acidic buffer consists of a weak acid and its conjugate base (e.g.  $CH_3COOH$ ,  $CH_3COO^-$ ). There is a large amount of salt compared to a weak acid, to ensure that it can absorb the shock of addition of acid/alkali.

#### Option 1: Add excess weak acid to strong base

50cm<sup>3</sup> of 0.8 mol/dm<sup>3</sup> of Ethanoic acid is added to 30cm<sup>3</sup> of 0.5 mol/dm<sup>3</sup> of Potassium Hydroxide. Calculate pH of the buffer solution formed?  $K_a = 1.74 \times 10^{-5}$

	$CH_3COOH_{(aq)} + KOH_{(aq)} \longrightarrow CH_3COO^-K^+_{(aq)} + H_2O_{(aq)}$			
Initial Moles	0.04	0.015	0	0
Reacted or Formed	-0.015	-0.015	+0.015	+0.015
Final	0.025	0	0.015	0.015

This results in the below Buffer:

	$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$		
Moles:	0.025	0.015	
Total Volume:	80cm <sup>3</sup>	80cm <sup>3</sup>	
Concentration:	0.3125	0.1875	

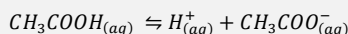
To calculate pH of Buffer, we use the  $K_a$  expression:

$$K_a = \frac{[H^+_{(aq)}][CH_3COO^-_{(aq)}]}{[CH_3COOH_{(aq)}]}$$
$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{(1.74 \times 10^{-5}) \times 0.3125}{0.1875} = 2.9 \times 10^{-5} \text{ mol/dm}^3$$
$$pH = -\log(2.9 \times 10^{-5}) = 4.54$$

#### Option 2: Adding salt containing conjugate base to weak acid.

Recall that the conjugate base in a weak acid is limited, which prevents it behaving as an acidic buffer. We can increase the amount of conjugate base within the weak acid by adding a salt such as  $CH_3COO^-Na^+$  to  $CH_3COOH$ . This then creates an acidic buffer.

Calculate the pH of the buffer solution formed when 2g of Sodium Ethanoate is added to 100cm<sup>3</sup> of 0.6mol/dm<sup>3</sup> Ethanoic acid.  $K_a = 1.74 \times 10^{-5}$



Calculate  $[CH_3COO^-Na^+]$ :

$$\text{Moles of } CH_3COO^-Na^+ = \frac{\text{Mass}}{\text{Mr}} = \frac{2}{82} = 0.024$$

Total Volume = 100cm<sup>3</sup>

$$\text{Concentration} = \frac{0.024 \times 1000}{100} = 0.24 \text{ mol/dm}^3$$

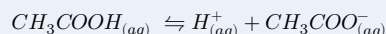
$$K_a = \frac{[H^+_{(aq)}][CH_3COO^-_{(aq)}]}{[CH_3COOH_{(aq)}]}$$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{(1.74 \times 10^{-5}) \times 0.6}{0.24} = 4.35 \times 10^{-5}$$

$$pH = -\log(4.35 \times 10^{-5}) = 4.36$$

## Calculating pH of buffer solution upon addition of small amounts of acid/alkali

You need to understand the above section on 'How an acidic buffer works' in order to be able to complete quantitative questions on this subject. Example of acidic buffer:



### Note:

- Effect of adding 0.01 mol acid ( $\text{H}^+$ ): 0.01 mol of  $\text{H}^+$  reacts with 0.01 mol of  $\text{CH}_3\text{COO}^-$  in buffer to form 0.01 mol of acid  $\text{CH}_3\text{COOH}$  in buffer. Hence, you subtract 0.01 mol from moles of  $\text{CH}_3\text{COO}^-$  in buffer, and add 0.01 mol to moles of  $\text{CH}_3\text{COOH}$  in buffer.
- Effect of adding 0.01 mol acid ( $\text{OH}^-$ ): 0.01 mol of  $\text{OH}^-$  reacts with 0.01 mol of  $\text{H}^+$  in buffer. To replace the lost  $\text{H}^+$ , the eqm shifts to the right (more acid dissociates). Hence, you subtract 0.01 mol from moles of  $\text{CH}_3\text{COOH}$  and add 0.01 mol to  $\text{CH}_3\text{COO}^-$ .
- This slight change in moles/concentration in acid/conjugate base, will result in a very small change in pH, that can be considered as relatively constant.

### E.g.12

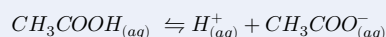
1000cm<sup>3</sup> of a buffer solution consisting of ethanoic acid and ethanoate ions has a pH of 4.58 and has the following specification:

$$[\text{CH}_3\text{COOH}] = 0.15 \text{ mol/dm}^3$$

$$[\text{CH}_3\text{COO}^-] = 0.10 \text{ mol/dm}^3$$

$$K_a = 1.74 \times 10^{-5}$$

Calculate the pH of buffer solution post addition of 10cm<sup>3</sup> of 1 mol/dm<sup>3</sup> Hydrochloric acid?



- 1) First calculate original moles of ethanoic acid and ethanoate ions in the buffer solution:

$$\text{Moles of Ethanoic Acid} = \frac{C \times V}{1000} = \frac{0.15 \times 1000}{1000} = 0.15 \text{ moles}$$

$$\text{Moles of Ethanoate} = \frac{C \times V}{1000} = \frac{0.10 \times 1000}{1000} = 0.10 \text{ moles}$$

- 2) Calculate moles of acid added to buffer solution:

$$\text{Moles of } \text{H}^+ \text{ added} = \frac{C \times V}{1000} = \frac{1 \times 10}{1000} = 0.01 \text{ moles}$$

- 3) Moles of buffer constituents post addition of acid:

$$\text{New moles of } \text{CH}_3\text{COOH} = 0.15 + 0.01 = 0.16 \text{ moles}$$

$$\text{New moles of } \text{CH}_3\text{COO}^- = 0.10 - 0.01 = 0.09 \text{ moles}$$

- 4) Prior to plugging these into the  $K_a$  expression, we require for the above new moles to be converted to concentration. Note, new volume of buffer is 1010cm<sup>3</sup>:

$$\text{Concentration of } \text{CH}_3\text{COOH} = \frac{n \times 1000}{V} = \frac{0.16 \times 1000}{1010} = 0.158 \text{ mol/dm}^3$$

$$\text{Concentration of } \text{CH}_3\text{COO}^- = \frac{n \times 1000}{V} = \frac{0.09 \times 1000}{1010} = 0.089 \text{ mol/dm}^3$$

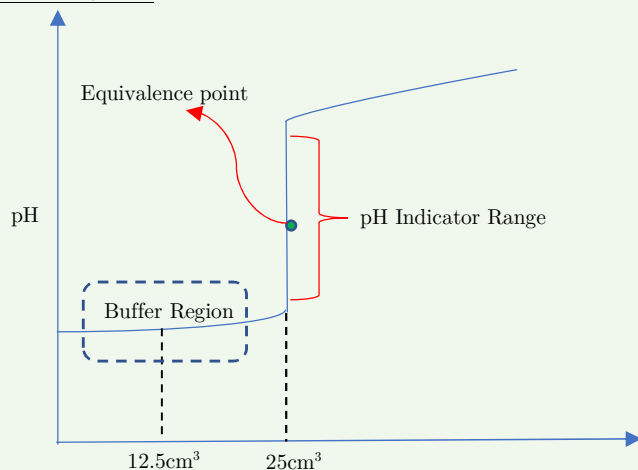
$$K_a = \frac{[\text{H}^+_{(aq)}][\text{CH}_3\text{COO}^-_{(aq)}]}{[\text{CH}_3\text{COOH}_{(aq)}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{(1.74 \times 10^{-5}) \times 0.158}{0.089} = 3.089 \times 10^{-5} \text{ mol/dm}^3$$

$$\text{pH} = -\log(3.089 \times 10^{-5}) = 4.51$$

## Weak acid vs Strong Base Titration

### Titration Curves



### Note:

25cm<sup>3</sup>: Neutralisation point

12.5cm<sup>3</sup>: Half Neutralisation point

Prior to the neutralisation point, there is excess weak acid being reacted with strong base. Recall: Excess weak acid + strong base results in an acidic buffer. Therefore, this region is referred to as buffer region.

### Note:

At half neutralisation point:

$$[\text{HA}] = [\text{A}^-]$$

Therefore, the  $K_a$  expression will simplify to:

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

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

Applying the log function to both sides:

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

On the titration curve to the left, at the half neutralisation point, the pH of the solution will equal to the  $\text{p}K_a$ .