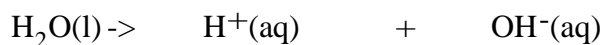


# SOLUTIONS

## Equilibrium in Water

Water is a very weak acid i.e. it is a proton  $H^+$  donor:



$OH^-$  is referred to as the 'conjugate base' of the acid  $H_2O$  - the species formed when the acid loses a proton.

The  $OH^-$  ion is a base i.e. it is a proton acceptor:



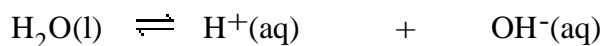
$H_2O$  is referred to as the 'conjugate acid' of the base  $OH^-$  - the species formed when the base gains a proton.

Notice that the  $H^+$  ion does not actually exist in water:  
 $H^+$  reacts with  $H_2O$  forming the hydroxonium ion  $H_3O^+$ :

$$H^+ + H_2O \rightarrow H_3O^+$$

For simplicity we will continue to use  $H^+$  to represent  $H_3O^+$ .

The following equilibrium exists in Water:



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

$K_a$  is known as the acid dissociation constant.

Since Water is only very slightly ionised,  $[H_2O]$  is effectively a constant, therefore the product  $K_a[H_2O]$  is also a constant,  $K_w$ :

$$K_a[H_2O] = K_w = [H^+][OH^-]$$

$$[H^+] = [OH^-] = 10^{-7} \text{ mol l}^{-1}$$

Therefore:

$$K_w = [10^{-7}][10^{-7}] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

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

N.B.  $pOH = -\log[OH^-] = -\log(10^{-7}) = 7$

$$pOH + pH = 14$$

## Equilibrium in Ethanoic acid

The following equilibrium exists in Ethanoic acid:



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

Since  $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

$$\Rightarrow [\text{H}^+]^2 = K_a[\text{CH}_3\text{COOH}]$$

$$\Rightarrow 2\log[\text{H}^+] = \log K_a + \log[\text{CH}_3\text{COOH}]$$

$$\Rightarrow -\log[\text{H}^+] = -1/2\log K_a - 1/2\log[\text{CH}_3\text{COOH}]$$

$$\Rightarrow \text{pH} = -1/2\log K_a - 1/2\log[\text{CH}_3\text{COOH}]$$

If we define  $\text{p}K_a = -\log K_a$  then

$$\text{pH} = 1/2\text{p}K_a - 1/2\log[\text{CH}_3\text{COOH}]$$

**Problem:** Calculate the pH of a 0.3M solution of Ethanoic acid in water.  
 $[K_a \text{ for Ethanoic acid} = 1.7 \times 10^{-5} \text{ mol l}^{-1}]$

$$\begin{aligned} \text{Answer: } \text{pH} &= -1/2 \log K_a - 1/2 \log[\text{CH}_3\text{COOH}] \\ &= -1/2 \log(1.7 \times 10^{-5}) - 1/2 \log(0.3) \\ &= -1/2 (-4.77) - 1/2 (-0.52) \\ &= 2.39 + 0.26 \\ &= \underline{2.65} \end{aligned}$$

**Problem:** Calculate the pH of a 0.15 M solution of Propanoic acid in water.  
[pK<sub>a</sub> for Propanoic acid = 4.9]

$$\begin{aligned}
 \text{Answer: } \text{pH} &= 1/2 \text{pK}_a - 1/2 \log [\text{CH}_3\text{CH}_2\text{COOH}] \\
 &= 1/2(4.9) - 1/2 \log(0.15) \\
 &= 2.45 - 1/2(-0.82) \\
 &= 2.45 + 0.41 \\
 &= \underline{2.86}
 \end{aligned}$$

**Problem:** Calculate the [H<sup>+</sup>] in a 0.2 mol l<sup>-1</sup> solution of Ammonium chloride NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup> in water.  
[K<sub>a</sub> for the Ammonium ion = 5.6 x 10<sup>-10</sup>]

$$\begin{aligned}
 \text{Answer: } \text{NH}_4^+ &\rightleftharpoons \text{NH}_3 + \text{H}^+ \\
 K_a &= \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \\
 &= \frac{[\text{H}^+]^2}{[\text{NH}_4^+]} \quad \text{Since } [\text{NH}_3] = [\text{H}^+] \\
 \Rightarrow [\text{H}^+] &= \sqrt{K_a [\text{NH}_4^+]} \\
 &= \sqrt{(5.6 \times 10^{-10} \times 0.2)} \\
 &= \underline{1.06 \times 10^{-5} \text{ mol l}^{-1}}
 \end{aligned}$$

N.B. The higher the value of K<sub>a</sub> the stronger the acid  
[See values in SQA data booklet page 12]

## Buffer Solutions

Buffer solutions maintain their pH whether acid or alkali is added to them.

### Acid Buffers

An 'acid buffer' consists of a solution of a weak acid and one of its salts e.g. a solution of Ethanoic acid and Sodium ethanoate.

This contains the equilibrium:



Added H<sup>+</sup> ions are immediately attacked by CH<sub>3</sub>COO<sup>-</sup> ions and so do not lower the pH.

Added OH<sup>-</sup> ions are immediately attacked by CH<sub>3</sub>COOH molecules and so do not raise the pH.

**Problem:** Calculate the pH of a buffer solution containing  
0.01 mol l<sup>-1</sup> Ethanoic acid and 0.05 mol l<sup>-1</sup> Sodium ethanoate.  
[pK<sub>a</sub> for Ethanoic acid = 4.8]



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

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

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

$$= -\log \left( \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right)$$

$$= -\log K_a - \log \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right)$$

$$= \text{p}K_a - \log \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right)$$

$$= 4.8 - \log \left( \frac{0.01}{0.05} \right)$$

$$= 4.8 - \log (0.2)$$

$$= 4.8 + 0.7$$

$$= \underline{5.5}$$

**Problem:** You are required to make 1000 cm<sup>3</sup> of an acid buffer solution of pH 5 using a 0.1 mol l<sup>-1</sup> solution of Sodium ethanoate and a 0.2 mol l<sup>-1</sup> solution of Ethanoic acid. What volumes of each solution would be required?  
[pK<sub>a</sub> for Ethanoic acid = 4.8]

**Answer:**

$$\text{pH} = \text{pK}_a - \log\left(\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}\right)$$

$$\Rightarrow \log\left(\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}\right) = \text{pK}_a - \text{pH}$$

$$= 4.8 - 5$$

$$= -0.2$$

$$\Rightarrow \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 0.63$$

Let the volume of CH<sub>3</sub>COOH required be x cm<sup>3</sup>

Let the volume of CH<sub>3</sub>COO<sup>-</sup> required be y cm<sup>3</sup>

$$x + y = 1000 \quad \dots\dots\dots\text{equation 1}$$

$$[\text{CH}_3\text{COOH}] = \frac{0.2x}{1000}$$

$$[\text{CH}_3\text{COO}^-] = \frac{0.1y}{1000}$$

$$\Rightarrow \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{2x}{y}$$

$$\Rightarrow \frac{2x}{y} = 0.63 \quad \dots\dots\dots\text{equation 2}$$

Solving equations 1 and 2 gives the answer:

$$\text{Volume of CH}_3\text{COOH} \quad x = 240 \text{ cm}^3$$

$$\text{Volume of CH}_3\text{COO}^- \quad y = 760 \text{ cm}^3$$

## Basic Buffers

A 'basic buffer' consists of a solution of a weak base and one of its salts e.g. a solution of Ammonia and Ammonium chloride.

This contains the equilibrium:

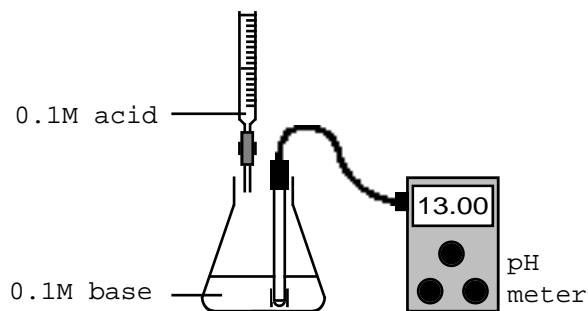


Added H<sup>+</sup> ions are immediately attacked by NH<sub>3</sub> molecules and so do not lower the pH.

Added OH<sup>-</sup> ions are immediately attacked by NH<sub>4</sub><sup>+</sup> ions and so do not raise the pH.

## Acid-Base Titrations

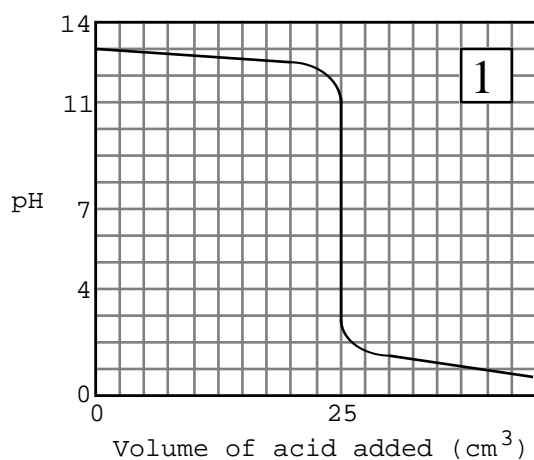
In all the examples which follow, a pH meter is used to measure the changes in pH which occur as 0.1M acid is titrated into 25 cm<sup>3</sup> 0.1M base.



The following curves show the changes in pH with volume of acid added.

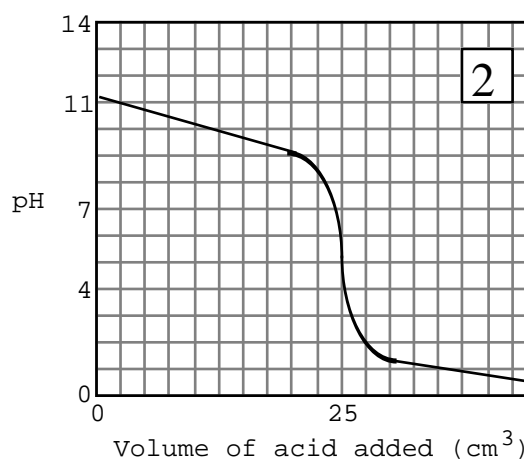
**Strong acid (HCl)**

**Strong base (NaOH)**



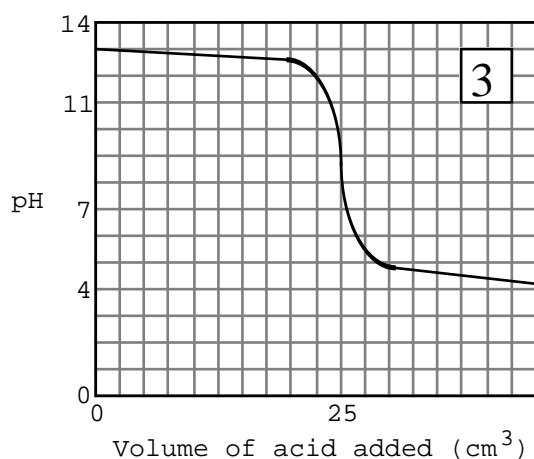
**Strong acid (HCl)**

**Weak base (NH<sub>3</sub>)**



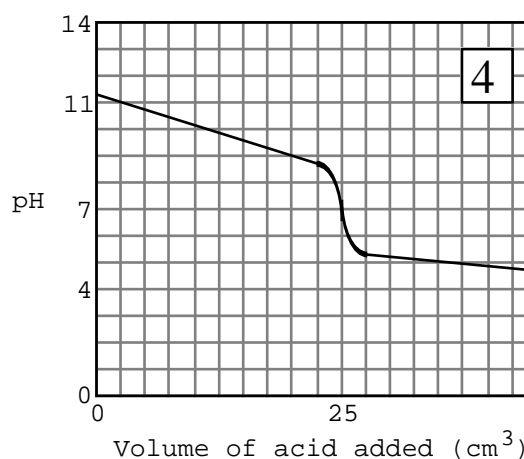
**Weak acid (CH<sub>3</sub>COOH)**

**Strong base (NaOH)**



**Weak acid (CH<sub>3</sub>COOH)**

**Weak base (NH<sub>3</sub>)**



In all graphs note:-

- The region of buffering at the start of the titration when [base] is high. As the acid is added the H<sup>+</sup> ions are immediately wiped out by the excess base so there is little change in pH.
- The pH changes most rapidly around the end point.
- The slow rate of change of pH at the end of the titration. Here, acid is being added to acid of the same concentration so [H<sup>+</sup>] changes very little.

**Curve 1:** Strong acid (HCl) / Strong base (NaOH)

The salt formed at the end point is NaCl. Since this is the salt of a strong acid/strong base the pH is 7.

**Curve 2:** Strong acid (HCl)/Weak base (NH<sub>3</sub>)

The salt formed at the end point is NH<sub>4</sub>Cl. Since this is the salt of a strong acid/weak base the pH is 3 - 5.

**Curve 3:** Weak acid (CH<sub>3</sub>COOH) / Strong base (NaOH)

The salt formed at the end point is CH<sub>3</sub>COONa. Since this is the salt of a weak acid/strong base the pH is 9 - 11.

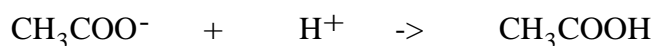
**Curve 4:** Weak acid (CH<sub>3</sub>COOH)/Weak base (NH<sub>3</sub>)

The salt formed at the end point is CH<sub>3</sub>COONH<sub>4</sub> (Ammonium ethanoate)

The ions present at the end point are, therefore:



Since CH<sub>3</sub>COOH is a weak acid, CH<sub>3</sub>COO<sup>-</sup> and H<sup>+</sup> tend to combine:



Since NH<sub>3</sub> is a weak base NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> tend to combine:



Since K<sub>a</sub>(CH<sub>3</sub>COOH) is approximately equal to K<sub>b</sub>(NH<sub>3</sub>), both H<sup>+</sup> and OH<sup>-</sup> are removed to the same extent so their concentrations remain equal and pH = 7.





For Phenol Red,  $pK_{In} = 7.9$  so it would be suitable for a strong acid/strong base titration (curve 1) but not for a strong acid/weak base titration (curve 2) - the colour would change around  $pH = 7.9$ , well before the end point at around  $pH = 5$  !

The table below lists the  $pK_{In}$  for some other indicators:

<b>Indicator</b>	<b><math>pK_{In}</math></b>	<b>Colour in acid</b>	<b>Colour in alkali</b>
Methyl Red	5.0	Red	Yellow
Bromothymol Blue	7.0	Yellow	Blue
Phenolphthalein	9.3	Colourless	Red

From the examples in the table it can be seen that

- All three indicators are suitable for a strong acid/strong base titration.
- Only Methyl Red is suitable for a strong acid/weak base titration.
- Only Phenolphthalein is suitable for a weak acid/strong base titration.
- None of the indicators is suitable for a weak acid/weak base titration as the  $pH$  does not change rapidly enough at the end point.