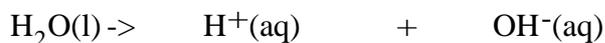


SOLUTIONS

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:



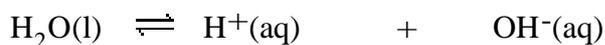
H_2O is referred to as the 'conjugate acid' of the base OH^- - the species formed when the base gains a proton.

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_a 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⁺] in a 0.2 mol l⁻¹ solution of Ammonium chloride NH₄⁺Cl⁻ in water.
[K_a for the Ammonium ion = 5.6 x 10⁻¹⁰]

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

N.B. The higher the value of K_a 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⁺ ions are immediately attacked by CH₃COO⁻ ions and so do not lower the pH.

Added OH⁻ ions are immediately attacked by CH₃COOH molecules and so do not raise the pH.

Problem: Calculate the pH of a buffer solution containing
0.01 mol l⁻¹ Ethanoic acid and 0.05 mol l⁻¹ Sodium ethanoate.
[pK_a 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 cm³ of an acid buffer solution of pH 5 using a 0.1 mol l⁻¹ solution of Sodium ethanoate and a 0.2 mol l⁻¹ solution of Ethanoic acid. What volumes of each solution would be required?
[pK_a 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 CH₃COOH required be x cm³

Let the volume of CH₃COO⁻ required be y cm³

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

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

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

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

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

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:

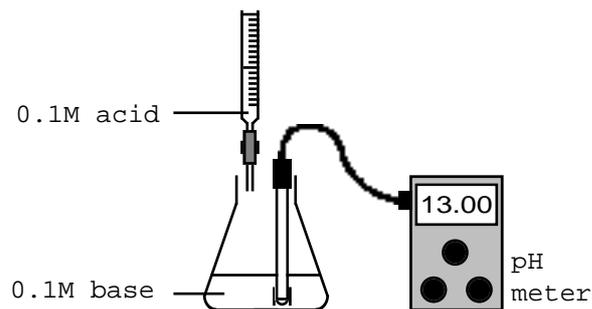


Added H⁺ ions are immediately attacked by NH₃ molecules and so do not lower the pH.

Added OH⁻ ions are immediately attacked by NH₄⁺ ions and so do not raise the pH.

Acid-Base Titrations

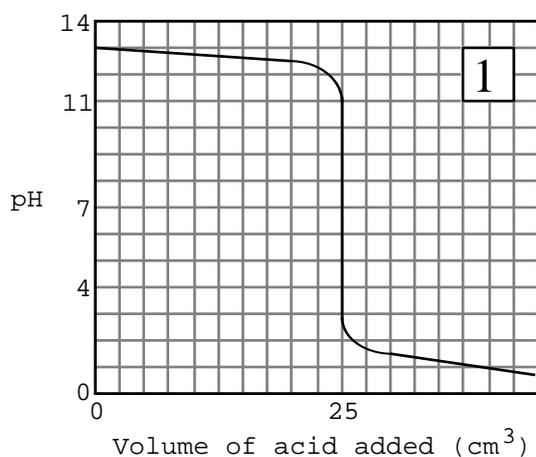
In all the examples which follow, a pH meter is used to measure the changes in pH which occur as 0.1M acid is titrated into 25 cm³ 0.1M base.



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

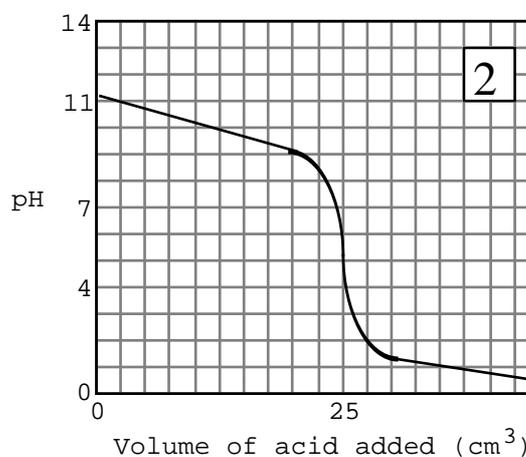
Strong acid (HCl)

Strong base (NaOH)



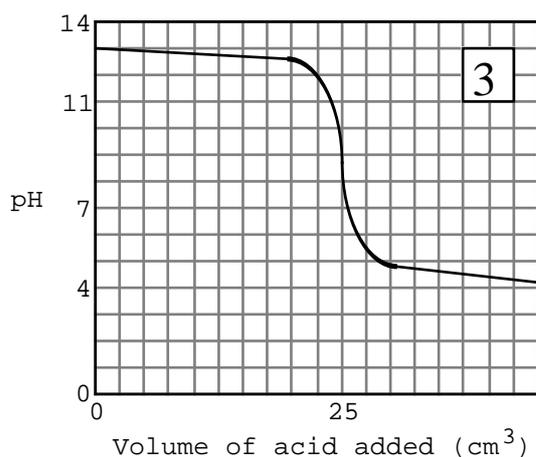
Strong acid (HCl)

Weak base (NH₃)



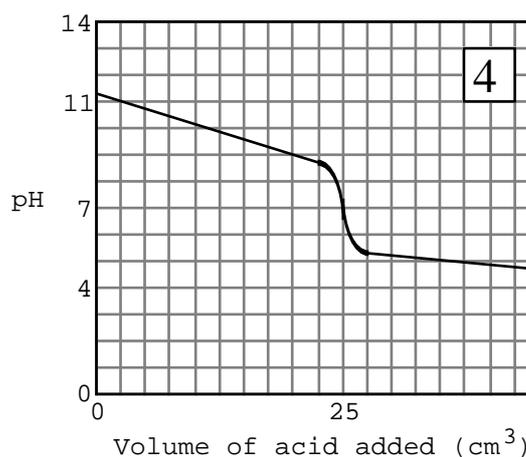
Weak acid (CH₃COOH)

Strong base (NaOH)



Weak acid (CH₃COOH)

Weak base (NH₃)



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⁺ 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⁺] 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 (NH₃)

The salt formed at the end point is NH₄Cl. Since this is the salt of a strong acid/weak base the pH is 3 - 5.

Curve 3: Weak acid (CH₃COOH) / Strong base (NaOH)

The salt formed at the end point is CH₃COONa. Since this is the salt of a weak acid/strong base the pH is 9 - 11.

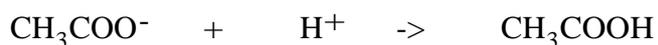
Curve 4: Weak acid (CH₃COOH)/Weak base (NH₃)

The salt formed at the end point is CH₃COONH₄ (Ammonium ethanoate)

The ions present at the end point are, therefore:



Since CH₃COOH is a weak acid, CH₃COO⁻ and H⁺ tend to combine:



Since NH₃ is a weak base NH₄⁺ and OH⁻ tend to combine:



Since K_a(CH₃COOH) is approximately equal to K_b(NH₃), both H⁺ and OH⁻ 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:

Indicator	pK_{In}	Colour in acid	Colour in alkali
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.