

## Acid-Base Equilibria II - Buffer Solutions, Titrations & Indicators

To succeed in this topic you need to:

- Ensure you understand Le Chatelier's Principle and the effect of changing conditions on the position of equilibrium (covered in Factsheet No.21)
- Review the work in Factsheet No. 25 because it is the first part of the whole work covering Acid-Base Equilibria
- be able to use your calculator to convert numbers into logarithms to the base 10 ( $\log_{10}$ ) using the **lg** key

After working through this Factsheet you will be able to:

- define buffer solutions and explain how they operate
- perform calculations on buffer solutions
- sketch the pH graphs for titrations of acids and bases
- identify which indicators to use for particular acid/base titrations

### Buffer Solutions



A buffer solution is one whose pH hardly changes on the addition of small amounts of acid or base

#### What are they?

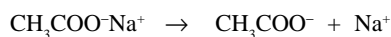
A buffer solution is a weak acid or base and its salt i.e. an acid/base conjugate pair.

e.g.  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^- \text{Na}^+$  (which gives a pH in the acidic range)

e.g.  $\text{NH}_3/\text{NH}_4\text{Cl}$  (which produces a pH in the basic range)

#### How do they work?

If we look at the example of ethanoic acid and sodium ethanoate then the salt is fully ionised:



The weak acid partially ionises,



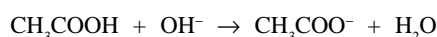
The  $\text{CH}_3\text{COO}^-$  from the salt mixed in the equilibrium mixture means  $[\text{CH}_3\text{COO}^-]$  is large and pushes the equilibrium to the left making  $[\text{CH}_3\text{COOH}]$  large as well. the  $[\text{H}^+]$  determines the pH of the buffer since  $\text{pH} = -\log_{10}[\text{H}^+]$ .

If an **acid** is added i.e.  $\text{H}^+$ , then almost all of the  $\text{H}^+$  ions are removed by the  $\text{CH}_3\text{COO}^-$ ,



leaving the  $[\text{H}^+]$  hardly changed (the  $[\text{CH}_3\text{COO}^-]$  is large).

If a **base** is added the  $\text{CH}_3\text{COOH}$  reacts with the  $\text{OH}^-$ .



but the  $[\text{CH}_3\text{COOH}]$  hardly changes because it is **large**.

### Calculations on buffer solutions

The calculations depend on a mathematical formula,



$$\text{pH} = -\log_{10} K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$$

or

$$\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$$

In examination questions you may be given the  $K_a$  or the  $\text{p}K_a$  value,

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

in the same way that

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

You must learn **both** the variations of the formula.

The two types of buffer solution calculations are:

#### 1. Finding pH - given the $K_a$ value and the concentrations of the acid and base.

What is the pH of a buffer solution of 0.10 mol  $\text{dm}^{-3}$  propanoic acid ( $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ ) and 0.20 mol  $\text{dm}^{-3}$  sodium propanoate ( $\text{C}_2\text{H}_5\text{CO}_2\text{Na}$ )?  $K_a$  for propanoic acid is  $1.34 \times 10^{-5}$  mol  $\text{dm}^{-3}$ .

**Answer** 
$$\text{pH} = -\log_{10} K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$$

$$\text{pH} = -\log_{10} 1.34 \times 10^{-5} - \log_{10} \frac{[0.1]}{[0.2]}$$

$$\begin{aligned} \text{pH} &= 4.87 - \log_{10} 0.5 \\ &= 4.87 + 0.30 = \mathbf{5.17} \end{aligned}$$

#### 2. Finding $K_a$ - given the pH value and the concentrations of the acid and the base.

0.01 mol  $\text{dm}^{-3}$  ethanoic acid is mixed with 0.117 mol  $\text{dm}^{-3}$  sodium ethanoate to produce a buffer solution of  $\text{pH} = 5.8$ . What is the  $K_a$  of the ethanoic acid?

**Answer**

$$\text{pH} = -\log_{10} K_a - \log_{10} \frac{[\text{acid}]}{[\text{base}]}$$

$$5.8 = -\log_{10} K_a - \log_{10} \frac{[0.01]}{[0.117]}$$

$$5.8 = -\log_{10} K_a - \log_{10} 0.0855$$

$$5.8 = -\log_{10} K_a + 1.068$$

$$\log_{10} K_a = -4.732$$

$$K_a = 1.85 \times 10^{-5} \text{ mol dm}^{-3}$$

If  $\log_{10} K_a = -4.732$ , you need to use

**SHIFT** **LOG** -4.732 to find  $K_a$

**Titration curves**

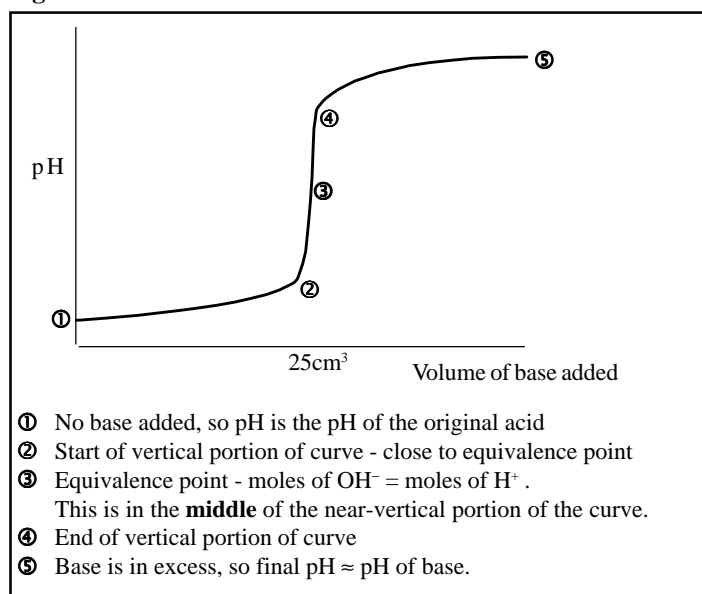
In the titration of an acid and a base, the pH changes during the course of the titration. In the laboratory the titration is stopped when the indicator changes colour at the end point. In titration curves the pH is measured as the acid and base are added together, and this continues past the end point.

We will consider here only monobasic acids and bases - i.e. acids (HA) that have only one hydrogen ion and bases (BOH) that have only one hydroxide ion - the titration curves for other kinds of acids are substantially more complicated.

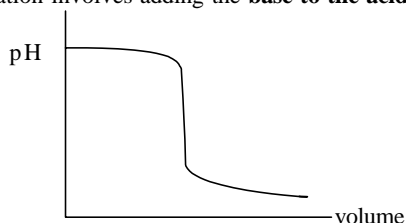
**What does a titration curve look like?**

For the sake of simplicity, it will be assumed that the acid and base are of the same concentration, and that 25cm<sup>3</sup> of the acid is used initially. The equivalence point (the point at which the acid and base exactly neutralise each other) will then be when 25cm<sup>3</sup> of the base has been added.

Fig 1 below shows a general titration curve, which shows how the pH varies with the volume of base added.

**Fig 1. Titration curve**

If instead the titration involves adding the **base to the acid** the graph is reversed:



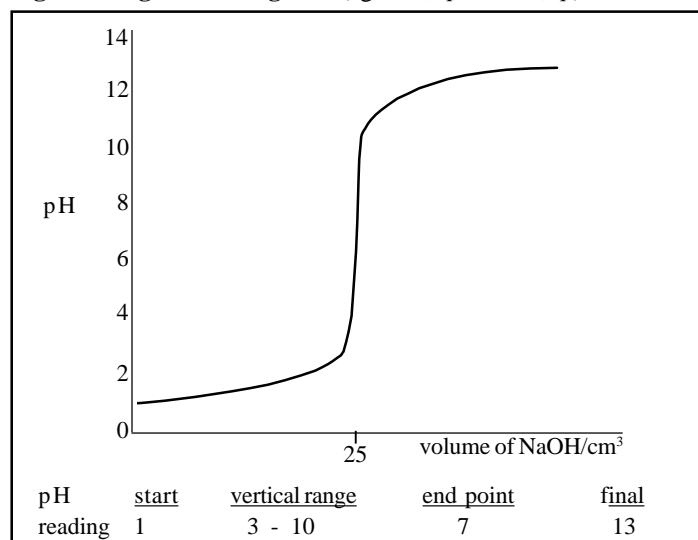
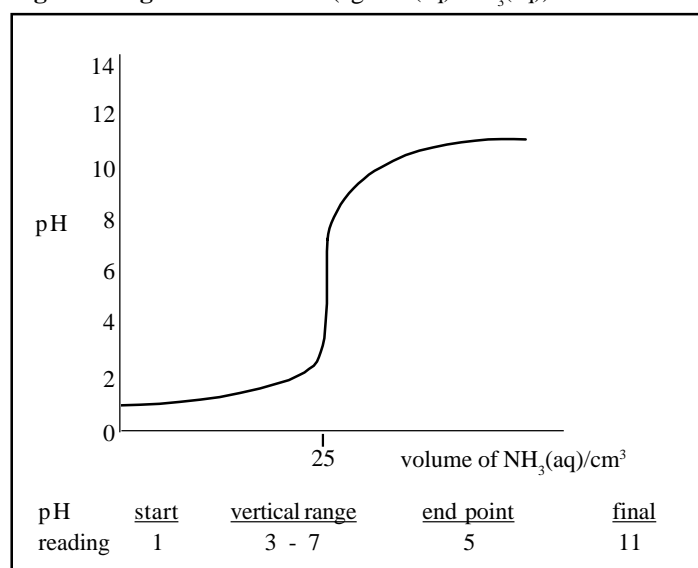
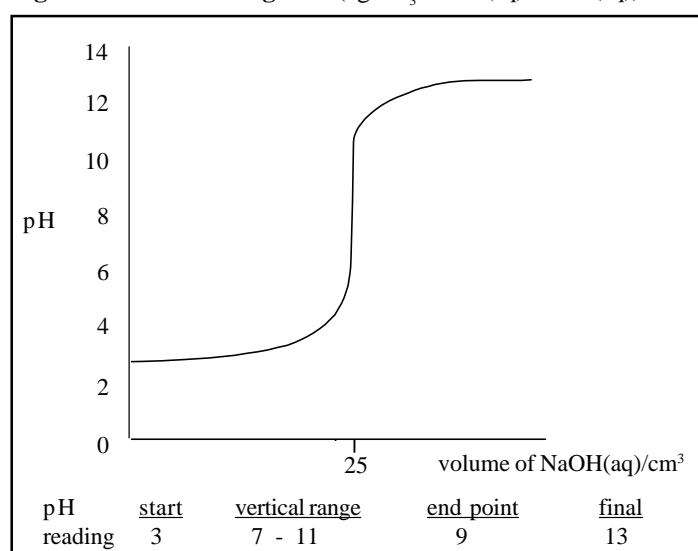
There are three curves you need to learn and be able to draw yourself:

1. Strong acid/strong base (Fig 2)
2. Strong acid/weak base (Fig 3)
3. Weak acid/strong base (Fig 4)

For each of these, you need to know approximate figures for:

- The pH at the start and end of the titration
- The pH range for the vertical part of the graph
- The equivalence point (*note: this is only pH 7 for a strong acid and strong base*)

NB. There is no titration between a weak acid and a weak base because there is no vertical range so no sharp end point (indicators do not show a clear colour change.)

**Fig 2. Strong acid/strong base (eg HCl(aq)/NaOH(aq))****Fig 3. Strong acid/weak base (eg HCl(aq)/NH<sub>3</sub>(aq))****Fig 4. Weak acid/strong base (eg CH<sub>3</sub>COOH(aq)/NaOH(aq))**

**Why do titration curves have that shape?**

- At the beginning of the titration, there is very little base compared to the acid, so the pH does not change much.
- As the equivalence point approaches, there are comparatively few  $H^+$  ions remaining, so the addition of a small amount of  $OH^-$  ions can cause the pH to change a great deal.
- Once the base is present in excess, addition of further  $OH^-$  ions only causes a small change in pH.

This shape can also be verified using pH calculations. The examples below show how to do them for a titration between  $25\text{cm}^3$   $0.1\text{M}$  hydrochloric acid and  $0.1\text{M}$  sodium hydroxide. **Note: you will not have to work out the shape using calculations in the exam.**

(a) To calculate pH before equivalence point:

When  $24.9\text{cm}^3$  of NaOH has been added, we have:

$$0.025 \times 0.1 = 0.0025 \text{ moles of } H^+$$

$$0.0249 \times 0.1 = 0.00249 \text{ moles of } OH^-$$

$$\text{contained in } 25 + 24.9 = 49.9\text{cm}^3$$

So we have  $0.0025 - 0.00249 = 0.00001$  moles of  $H^+$  ions left contained in  $49.9\text{cm}^3$

$$\text{This gives } [H^+] = 0.00001/0.0499 = 0.0002\text{M}$$

$$\text{So pH} = -\log_{10}(0.0002) = 3.7$$

(b) To calculate pH after equivalence point:

When  $25.1\text{cm}^3$  of NaOH has been added, we have:

$$0.025 \times 0.1 = 0.0025 \text{ moles of } H^+$$

$$0.0251 \times 0.1 = 0.00251 \text{ moles of } OH^-$$

$$\text{contained in } 25 + 25.1 = 50.1\text{cm}^3$$

So we have  $0.00251 - 0.0025 = 0.00001$  moles of  $OH^-$  ions contained in  $50.1\text{cm}^3$

$$\text{This gives } [OH^-] = 0.00001/0.0511 = 0.000196\text{M}$$

$$\text{Using } [H^+][OH^-] = K_w = 10^{-14}:$$

$$[H^+] = 10^{-14}/0.000196 = 5.11 \times 10^{-11}$$

$$\text{pH} = 10.2$$

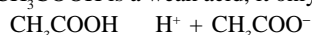
If you are happy with Excel Spreadsheets, you could use them to produce a titration curve for this example by putting the volume of sodium hydroxide added in the first column, and in the second column, entering the formula " $=\log((2.5 - 0.1*A1)/(25 + A1))$ " for volumes before the equivalence point, and " $=14 + \log(0.1*A1 - 2.5)/(25 + A1)$ " for volumes above the equivalence point.

**Why do weak acid/strong base and strong acid/weak base titrations have equivalence points that are not neutral?**

Consider a weak acid (ethanoic acid) titrated against a strong base (sodium hydroxide).

First note that for a weak acid like  $\text{CH}_3\text{COOH}$ , its conjugate base ( $\text{CH}_3\text{COO}^-$ ) will be weakly basic.

Since  $\text{CH}_3\text{COOH}$  is a weak acid, it only partially dissociates:

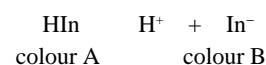


During the titration, the  $H^+$  ions will quickly be neutralised, causing the equilibrium above to shift to the right. At the equivalence point, there will be  $\text{CH}_3\text{COO}^-$  in solution, causing the pH to be slightly basic.

Similarly, for a weak base/strong base titration, since the conjugate acid of a weak base is slightly acidic, the equivalence point will have an acid pH.

**Indicators**

Indicators are weak acids and have the general formula,  $\text{HIn}$ . As with other weak acids they form an equilibrium in water where the anion,  $\text{In}^-$ , has one colour and the undissociated acid,  $\text{HIn}$ , another colour,



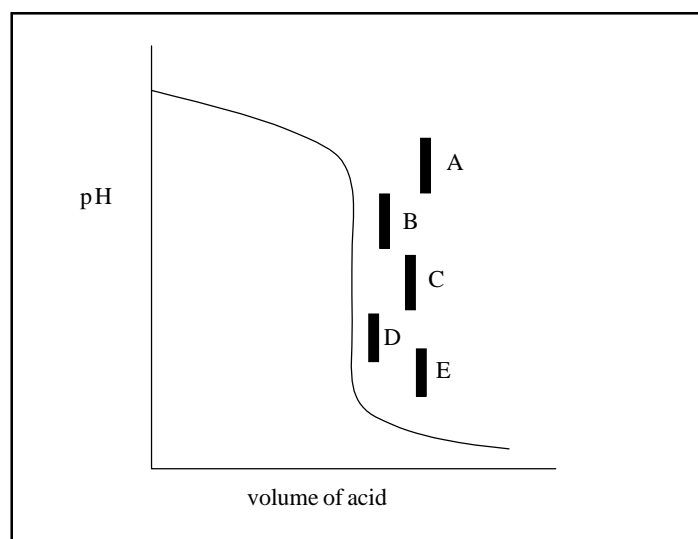
when  $H^+$  is added the equilibrium moves to the left and colour A is seen, adding a base produces colour B.

At equilibrium:  $[\text{HIn}] = [\text{In}^-]$

so the colour of the indicator is a 50%:50% mixture of colours A and B.

Different indicators are used for different combinations of strong and weak acids/bases. See Fig 5.

**Fig 5. Indicators**



The best indicator is C because it is closest to the mid point of the vertical pH change, but B and D would work as well. A and E will not change colour because they are outside the range of pH change. (Table 1)

**Table 1. Suitable indicators**

| Combination             | vertical change in pH | suitable indicator               |
|-------------------------|-----------------------|----------------------------------|
| strong acid/strong base | 3 – 10                | methyl orange or phenolphthalein |
| strong acid/weak base   | 3 – 7                 | methyl orange                    |
| weak acid/strong base   | 7 – 10                | phenolphthalein                  |

**Exam Hint:** - You may be given the pH range over which a number of indicators change colour, and be asked to identify which would be suitable for a specific titration. This requires you to be able to:

- Identify weak and strong acids and bases
- Recall the pH range for the vertical portion of the corresponding titration curve.

## Questions

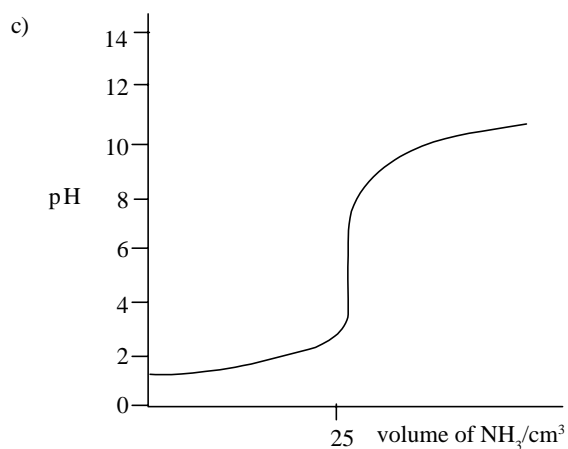
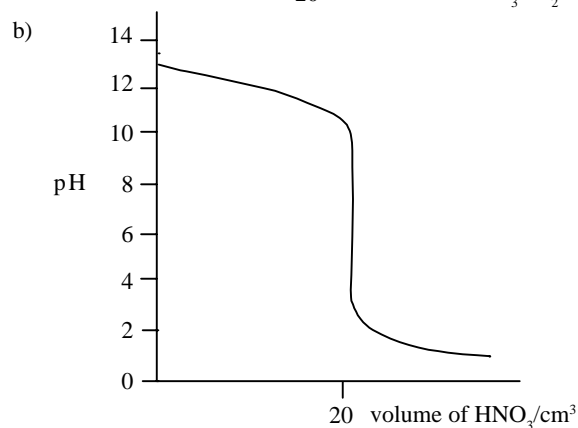
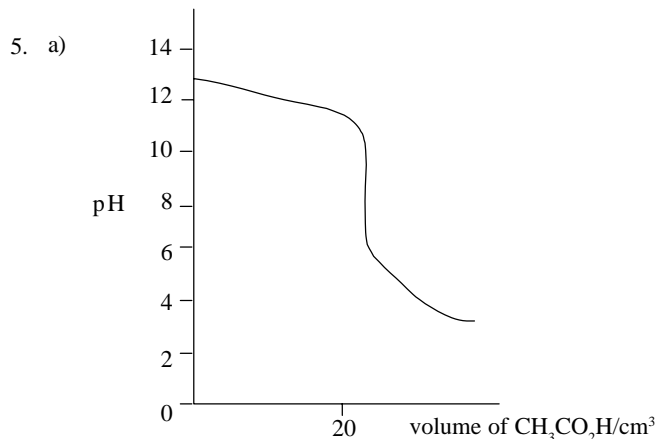
- What is a buffer solution?
  - How is a buffer solution made?
- For each of the following buffer solutions calculate its pH.
  - [acid] =  $0.1 \text{ mol dm}^{-3}$  [base] =  $0.05 \text{ mol dm}^{-3}$   
 $K_a = 1.3 \times 10^{-5} \text{ mol dm}^{-3}$
  - |      | [acid]/ $\text{mol dm}^{-3}$ | [base] $\text{mol dm}^{-3}$ |
|------|------------------------------|-----------------------------|
| i.   | 1.0                          | 1.0                         |
| ii.  | 2.0                          | 1.0                         |
| iii. | 2.0                          | 0.5                         |
| iv.  | 0.5                          | 2.0                         |

 The  $K_a = 1.5 \times 10^{-5} \text{ mol dm}^{-3}$  in each case.
  - |      | [acid]/ $\text{mol dm}^{-3}$ | [base] $\text{mol dm}^{-3}$ |
|------|------------------------------|-----------------------------|
| i.   | 0.10                         | 1.0                         |
| ii.  | 2.0                          | 0.2                         |
| iii. | 0.50                         | 2.5                         |
| iv.  | 0.85                         | 2.1                         |

 The  $K_a = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$  in each case.
- What is the  $K_a$  of the acid in each of the following questions?
  - $0.10 \text{ mol dm}^{-3}$  ethanoic acid with  $0.10 \text{ mol dm}^{-3}$  sodium ethanoate having a pH = 4.73?
  - $2.0 \text{ mol dm}^{-3}$  butanoic acid with  $0.50 \text{ mol dm}^{-3}$  sodium butanoate having a pH = 4.22?
  - $1.6 \text{ mol dm}^{-3}$  propanoic acid with  $1.2 \text{ mol dm}^{-3}$  potassium propanoate, having a pH of 4.75?
- Explain why a mixture of hydrochloric acid and sodium chloride does not act as a buffer solution, but a mixture of ethanoic acid and sodium ethanoate does.
- Draw the titration curves for each of the following:
  - $20 \text{ cm}^3$   $0.1 \text{ mol dm}^{-3}$  NaOH with  $0.1 \text{ mol dm}^{-3}$   $\text{CH}_3\text{CO}_2\text{H}$
  - $40 \text{ cm}^3$   $0.1 \text{ mol dm}^{-3}$  KOH with  $0.1 \text{ mol dm}^{-3}$   $\text{HNO}_3$
  - $25 \text{ cm}^3$   $0.1 \text{ mol dm}^{-3}$   $\text{HNO}_3$  with  $0.1 \text{ mol dm}^{-3}$   $\text{NH}_3(\text{aq})$
- Litmus is an indicator which is purple, and shows two colours red (with acids) and blue (with bases). Explain how litmus works.

## Answers

- A solution whose pH hardly changes when small amounts of acid or base are added to it.
  - A mixture of a weak acid and its salt, e.g.  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$
- 4.6
  - 4.8
    - 4.5
    - 4.2
    - 5.4
  - 4.8
    - 2.8
    - 4.5
    - 4.2
- $1.86 \times 10^{-5} \text{ mol dm}^{-3}$
  - $1.5 \times 10^{-5} \text{ mol dm}^{-3}$
  - $1.33 \times 10^{-5} \text{ mol dm}^{-3}$
- Hydrochloric acid is a strong acid, and so fully dissociates - there is no equilibrium between HCl and its ions



6. Litmus is a weak acid,  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$   
 red                      blue  
 (colours must be this way round)

*Acknowledgements: This Factsheet was researched and written by Sam Goodman. Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF. ChemistryFactsheets may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher. ISSN 1351-5136*