



## Acid Base III: Buffer solutions, pH Curves and Dibasic Acids

To succeed with this topic you need to understand the concepts of pH,  $K_a$ , buffers and pH curves. (Factsheets 25 and 26).

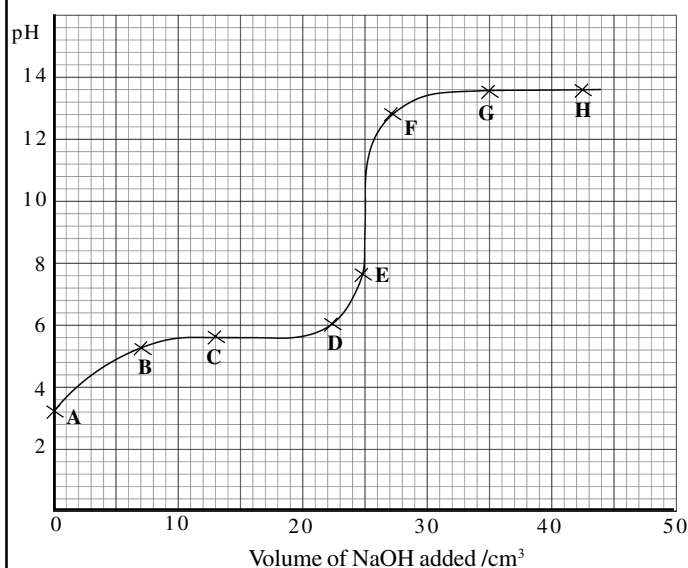
After working through this Factsheet you will:

- understand the link between buffer solutions and the pH curve for a weak acid with a strong base;
- be able to use the pH curve for a weak acid with a strong base to find  $pK_a$  and  $K_a$  for the weak acid involved;
- have met the pH 'problems' of  $H_2SO_4$ , a dibasic acid.

### Buffer solutions and pH curves

#### pH curves

The **pH curve** for the titration of a weak acid with a strong base has the shape shown below:



We need to look in more detail at what chemicals are in the solution mixture at various points on the curve (A-H):

- A pure weak acid (HA)
- B weak acid (HA) + some of its salt ( $A^-$ ) because of the neutralisation reaction between the acid and the alkali and more water because: acid + alkali  $\rightarrow$  salt + water
- C less weak acid (HA) and more salt ( $A^-$ )
- D even less weak acid (HA) and even more salt ( $A^-$ )
- E no weak acid left, the solution contains only the salt
- E-F the end-point where one drop of the base ( $A^-$ ) changes the solution from acidic to basic (pH 7  $\rightarrow$  11)
- F a salt solution + a slight excess of base (NaOH)
- G + H as an excess of base is added the pH increases to maximum value of about pH = 13.

**Exam Hint** : The three main points covered by this Factsheet are very common examination questions – learn this work thoroughly

#### Buffer solutions

1. A buffer solution is one whose **pH hardly changes** when **small amounts** of acid and alkali are added to it.
2. A buffer solution is made by dissolving the salt of a weak acid in the weak acid itself  
e.g. sodium ethanoate ( $CH_3COONa$ ) dissolved in ethanoic acid ( $CH_3COOH$ )
3. The following mathematical equation is used for buffer solutions:

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

or

$$pH = pK_a - \log_{10} \frac{[acid]}{[anion]}$$

N.B. 'p' =  $-\log_{10}$

We need to look at the **link** between this pH curve and buffer solutions.

**Reminder**: a buffer solution is a mix of a weak acid (HA) and its salt ( $A^-$ )

**Question** : Where does this mixture appear on the curve?

**Answer**: Between points A and E on the curve.

The 'acidic' part of a pH curve between a weak and a strong base is a mixture of the weak acid and its salt i.e. it has the properties of a buffer.

If, while adding the base, the experiment had been stopped at any point between A and E, the solution could have been used as a **buffer solution**.

**The pH of the buffer solutions could be found by 'reading' the y-axis at, say, points B, C and D.**

Note that pH of the buffer is higher, the greater the proportion of salt to acid.

Beyond the point E, no acid is left, only the salt, so the solution would no longer be a buffer.

We need to move to the equation for a buffer solution.

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

The [acid] is [HA] and the [anion] is [A<sup>-</sup>].

What happens when [HA] = [A<sup>-</sup>]?

$$\log_{10} \frac{[\text{HA}]}{[\text{A}^-]} = \log_{10} 1 = 0$$

This means the equation becomes

$$\text{pH} = \text{p}K_a - 0 \quad \text{i.e.}$$

$$\text{pH} = \text{p}K_a \quad \text{when } [\text{HA}] = [\text{A}^-]$$

**When does [HA] = [A<sup>-</sup>]?**

This happens **half-way** to the **equivalence point**.

In the example graph,

Equivalence point = 25 cm<sup>3</sup> NaOH(aq)

so At **12.50cm<sup>3</sup>** NaOH,

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

This is point C, where the pH is 5.6.

Using the equation,

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

then

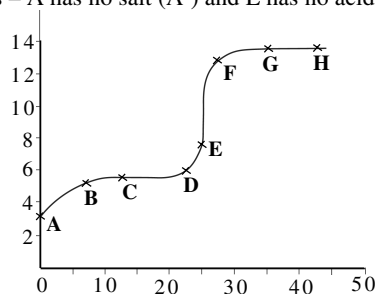
$$\text{p}K_a = -\log_{10} K_a$$

so the use of a calculator will enable us to **find K<sub>a</sub>**.

**Finding the value of K<sub>a</sub> for a weak acid from the pH curve** of a weak acid with a strong base:

- (1) The 'acid part' (up to the equivalence point) of the pH curve is a mixture of HA (weak acid) and its salt (A<sup>-</sup>),
- (2) A mixture of a weak acid (HA) and its salt (A<sup>-</sup>) is a buffer solution,
- (3) When [HA] = [A<sup>-</sup>] the mathematical equation for a buffer solution means pH = pK<sub>a</sub>
- (4) Reading the pH value from the graph at half the end point value (cm<sup>3</sup>) gives you the pK<sub>a</sub> value.
- (5) Using a calculator we can change pK<sub>a</sub> → K<sub>a</sub>.

N.B. From the example graph, point A and point E are not buffer solutions – A has no salt (A<sup>-</sup>) and E has no acid (HA).



The solution acts as a buffer at pH values of **more than 3 (A)** and **less than 7 (E)**.

Now the final test of your understanding!

**Question:** What is the pH range of the most effective buffer solution?

**Answer:** pH = 5.6 (C) to 6.8 (just below E)

**Reason:** This is when there is more of the anion, [A<sup>-</sup>] and less of the acid, [HA].

### Experimental methods of finding K<sub>a</sub> for a weak acid

Using the theory covered so far there are two methods to find K<sub>a</sub>:

#### Method 1

- (a) Pipette 25.00 cm<sup>3</sup> of the weak acid into a conical flask
- (b) Use a pH meter to measure its pH value.
- (c) Add 1.00cm<sup>3</sup> strong base (NaOH(aq)) from a burette, stir to mix and measure its pH value.
- (d) Continue to add 1.00cm<sup>3</sup> of NaOH(aq) and take the pH value readings.
- (e) Plot a graph of pH readings against the volume of NaOH(aq) added.
- (f) Use the graph to find the equivalence point (end point) in terms of cm<sup>3</sup> of NaOH(aq).
- (g) Divide the volume by 2.
- (h) Read off the pH value at end point volume ÷ 2 – this is the pK<sub>a</sub> value.
- (i) Convert pK<sub>a</sub> → K<sub>a</sub> using the calculator.

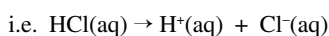
#### Method 2

- (a) Pipette 25.00cm<sup>3</sup> of the weak acid into a conical flask.
- (b) Add indicator.
- (c) Titrate with the strong base (NaOH(aq)) until the indicator changes colour, record the volume added.
- (d) Repeat the titration process until concordant titres are achieved.
- (e) Calculate from the titres the average titre – this will be the end point (equivalence point).
- (f) Divide the **average titre** by 2.
- (g) Pipette 25.00cm<sup>3</sup> of the weak acid into a conical flask.
- (h) Add the average titre volume of NaOH(aq), **divided by 2**.
- (i) Shake well and using a pH meter, find the pH value – this is the pK<sub>a</sub> value.
- (j) Convert pK<sub>a</sub> → K<sub>a</sub> using a calculator.

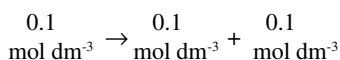
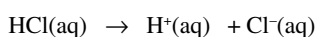
**The dibasic acid 'problem' of H<sub>2</sub>SO<sub>4</sub>**

H<sub>2</sub>SO<sub>4</sub> is a **strong acid**.

**Strong acids** are defined as ones which **fully dissociate** in solution,



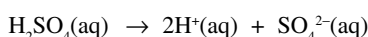
This fact enables us to calculate the **pH** of a **strong acid** from its **concentration**.

**Q. What is the pH of 0.1 mol dm<sup>-3</sup> HCl?**

$$[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(0.1) = 1.0$$

Suppose we take the same approach for H<sub>2</sub>SO<sub>4</sub>



$$[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(0.2) = 0.14$$

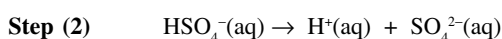
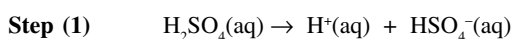
This suggests that H<sub>2</sub>SO<sub>4</sub> is **more** acidic (pH = 0.14) because it produces **twice** the number of H<sup>+</sup> ions.

**THIS IS NOT TRUE FOR H<sub>2</sub>SO<sub>4</sub>!**

When measured, the pH of 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is the same as for 0.1 mol dm<sup>-3</sup> HCl.

**Why is this?**

As a dibasic acid, sulphuric acid dissociates as shown below:



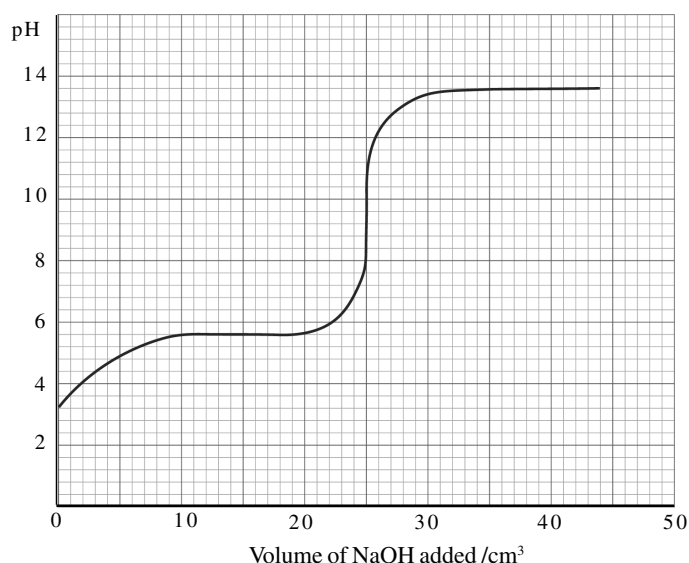
The key points are that:

- the dissociation constant for step (1) is very large - H<sub>2</sub>SO<sub>4</sub> completely dissociates into H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup>
- the dissociation constant for step (2) is small (about 0.01) - and this dissociation is also suppressed by the high H<sup>+</sup> concentration produced by step (1)

**Result** H<sub>2</sub>SO<sub>4</sub> only produces the same amount of ions as HCl so the pH value is about the same.

**Practice Questions**

1. The following questions are about the pH curve shown below when 25.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> HA(aq) was titrated with 1.0 mol dm<sup>-3</sup> NaOH(aq)



Use the pH curve to find

- the pH of the NaA(aq) solution.
  - for the weak acid, HA,
    - the pK<sub>a</sub> value
    - the K<sub>a</sub> value
  - the range of pH values over which the mixture acts as a buffer.
  - the pH of the most efficient buffer solution.
2. H<sub>2</sub>SO<sub>4</sub> is a strong dibasic acid, whereas HNO<sub>3</sub> is a strong monobasic acid. Why are the pHs of these two acids very similar?

**Answers**

- Any value between pH 8 → 11
  - 5.8
    - 1.58 × 10<sup>-6</sup>
  - 3.4 – 6.8
  - Any value between 5.8 – 7.8
- Answers gain credit for the following points:
  - Explanation of dibasic/monobasic acids in terms of the amount of H<sup>+</sup>/H<sub>3</sub>O<sup>+</sup> ions.
  - Explanation of strong acids (complete ionisation)
  - Compares HNO<sub>3</sub> (one H<sup>+</sup>) to H<sub>2</sub>SO<sub>4</sub> (two H<sup>+</sup>).
  - Links [H<sup>+</sup>] → pH value.
  - Explains that H<sub>2</sub>SO<sub>4</sub> has complete dissociation for H<sub>2</sub>SO<sub>4</sub> → H<sup>+</sup> + HSO<sub>4</sub><sup>-</sup> but only partial dissociation for HSO<sub>4</sub><sup>-</sup> → H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup>
  - Links the dissociation of acids to pH values i.e. similar because [H<sup>+</sup>] similar.

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