

## Determining the $pK_a$ of aspirin

### Student worksheet

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#### Health and safety note

Wear eye protection and ensure no naked flames.  $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution is an irritant. 95% ethanol is highly flammable. Aspirin and 95% ethanol are both harmful.

#### Principle

Aspirin is a weak acid. It partially ionises in water:



and its acid dissociation constant,  $K_a$ , is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

often written simply as:

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

The  $pK_a$  value is given by:

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

Taking logarithms, the following relationships are derived

$$\text{pH} = pK_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \quad \text{or} \quad \text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

When the acid is 'half-neutralised',  $[\text{A}^-] = [\text{HA}]$ , and  $\text{pH} = pK_a$ .

By titrating a solution of the aspirin against a strong alkali, such as sodium hydroxide solution, the pH at the half-way point can be determined and this gives the  $pK_a$  of aspirin.

Aspirin and sodium hydroxide react in a 1:1 mole ratio:



#### Equipment and materials

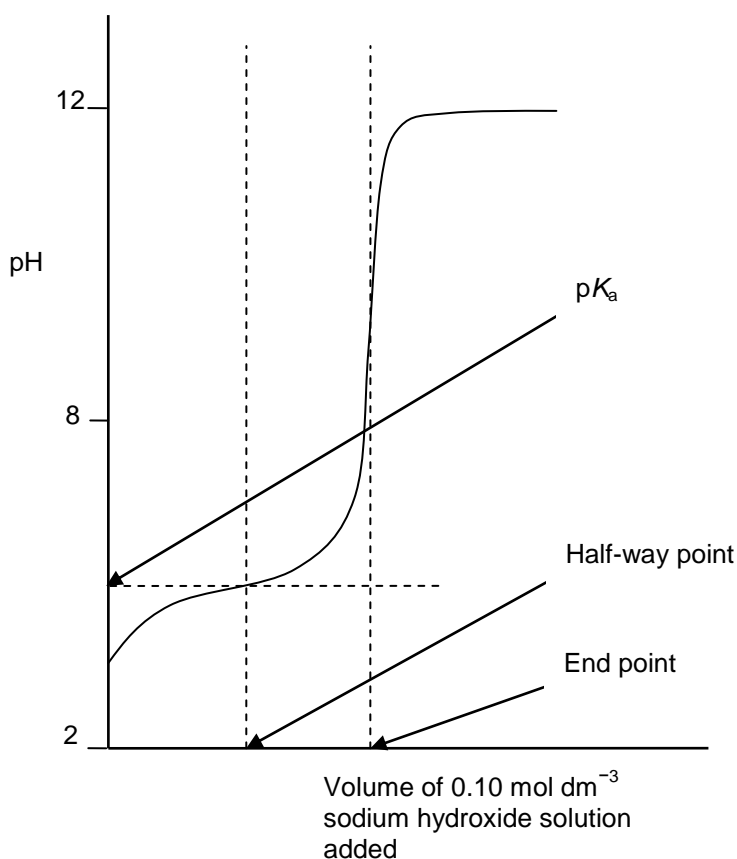
- Balance
- 50 cm<sup>3</sup> burette
- 250 cm<sup>3</sup> beaker
- Glass stirring rod
- 10 cm<sup>3</sup> and 100 cm<sup>3</sup> measuring cylinders
- Spatula
- pH probe and pH meter
- Aspirin – Harmful
- 95% ethanol – Highly flammable, Harmful
- $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution – Irritant

## Method

1. Fill a burette with  $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution.
2. Weigh  $0.36 \text{ g}$  of aspirin into a  $250 \text{ cm}^3$  beaker. Add  $10 \text{ cm}^3$  of 95% ethanol, Stir with a glass rod and when the solid has dissolved add  $90 \text{ cm}^3$  of deionised water. Stir the mixture until it is homogeneous.
3. Place a pH probe in the solution and connect it to a pH meter. Note: The pH probe should have been calibrated using suitable buffer solutions. (See Addendum)
4. Add  $2 \text{ cm}^3$  quantities of sodium hydroxide solution from the burette to the beaker, stirring well between additions and recording the pH.
5. Near the end-point the pH begins to rise rapidly. So after you have added  $18 \text{ cm}^3$  of sodium hydroxide solution begin adding it in  $0.5 \text{ cm}^3$  portions. After about  $22 \text{ cm}^3$  start adding in  $2 \text{ cm}^3$  portions again. Continue until total of  $36 \text{ cm}^3$  has been added.

## Processing data

1. Plot a graph of pH against volume of  $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution added.
2. From the graph, calculate the end-point of the titration.
3. Check this against the expected value by calculating the number of moles of aspirin used (relative molecular mass of aspirin = 180) and, therefore, the volume of  $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution needed to react with it in a 1:1 mole ratio.
4. From the graph, estimate the pH at the half-way point of the titration. This gives a value for the  $\text{p}K_{\text{a}}$  of aspirin.
5. Calculate the  $K_{\text{a}}$  of aspirin.



**Figure** Illustrative titration graph for aspirin against sodium hydroxide solution.

## Fliam pH Meter AP8673

### Specifications

Range: 0.00–14.00 pH

Accuracy: +0.2 pH

Resolution: 0.01 pH

Operating

Temperature: 0 °C–50 °C

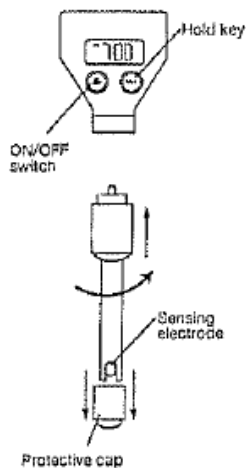
Calibration: One point, manual

Battery Supply: 3 × 1.5V  
(AG-13 battery)

Dimensions:

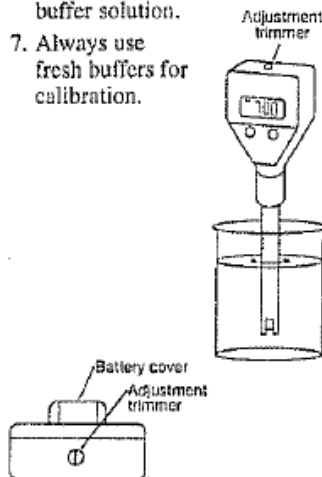
175 mm × 51 mm × 25 mm  
(7" × 2" × 1")

Weight: 57 g (2.0 oz)



### pH Calibration

1. Prior to use, remove the protective cap and condition the electrode by soaking the tip (bottom 4 cm/1½") in pH 7.00 standard buffer solution.
2. Stir gently and wait until the display stabilizes.
3. Use a small screw driver to adjust the calibration screw on the top of the pH meter until the display reads 7.00.
4. Rinse the electrode with distilled water and blot dry with filter paper.
5. Immerse the electrode in pH 4.00 or pH 10.00 standard buffer solution.
6. Once the display stabilizes (pH 4.00 or 10.00), approximately one minute, remove the pH meter from the buffer solution.
7. Always use fresh buffers for calibration.



### Operation

1. Remove the protective cap.
2. Rinse the electrode with distilled water and blot it dry with filter paper prior to use.
3. Turn the meter on by pressing the ON key.
4. Immerse the pH meter in the solution to be tested. *Never immerse the electrode up to the connector.*
5. Stir gently and wait for the reading to stabilize.
6. Press the "HOLD" key, the reading will be kept. When repeating a measurement, please press the "HOLD" key again, it automatically relieves the hold condition.
7. After use, rinse the electrode with distilled or deionized water to minimize contamination, blot dry.
8. Turn the meter off by pressing the OFF key.
9. Always replace the protective cap after use.