

## 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:

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

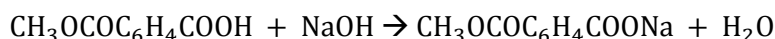
Taking logarithms, the following relationships are derived

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

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

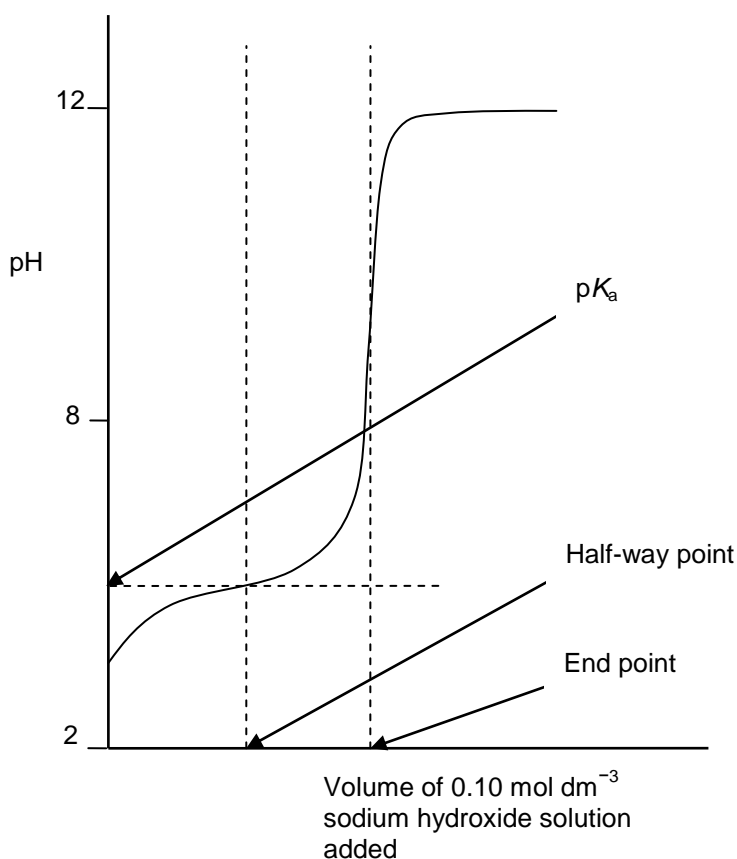
- Balance
- 50  $\text{cm}^3$  burette
- 250  $\text{cm}^3$  beaker
- Glass stirring rod
- 10  $\text{cm}^3$  and 100  $\text{cm}^3$  measuring cylinders
- Spatula
- pH probe and pH meter
- Aspirin – Harmful
- 95% ethanol – Highly flammable, Harmful
- $0.10 \text{ mol dm}^{-3}$  sodium hydroxide solution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