



21. On the acid trail

Introduction

Teachers who have not used the problems before should read the section *Using the problems* before starting.

Prior knowledge

Solution chemistry and in particular weak acids (K_a , pK_a and titration curves). A detailed knowledge is unnecessary as students are encouraged to consult textbooks and data books during the exercise.

Resources

Graph paper; data books and textbooks for reference; and scientific calculators should be available at the start of the exercise.

Group size

3.

Method

The equivalence point of the titration can be determined by plotting pH against volume of alkali added. This occurred at 15.00 cm³ of exactly 0.1 mol dm⁻³ NaOH.

The following information can now be determined:

1. Total acid (HA) concentration = $0.100 \times 15.00/25.0 = 0.0600 \text{ mol dm}^{-3}$
2. $pK_a = \text{pH}$ at half neutralisation = 4.20 (from graph)
therefore $K_a = 6.31 \times 10^{-5}$
3. pK_b of conjugate base (A) = $14 - 4.20$
= 9.80
therefore $K_b = 1.58 \times 10^{-10}$
4. The pH of the original solution (before any alkali is added) is found as follows:
 $K_a = [H^+][A^-]/[HA]$
 $[H^+]^2 = K_a \times [HA]$
= $6.31 \times 10^{-5} \times 0.0600$ (assuming that [HA] equals initial concentration of the acid)
 $[H^+] = 1.95 \times 10^{-3}$
 $\text{pH} = 2.71$
5. The degree of dissociation of the acid (α) before any alkali is added is given by:
 $\alpha = [H^+]/0.0600$
= 3.25×10^{-2}
6. The molar mass of the acid can be calculated as follows:
The original acid solution is 0.0600 mol dm⁻³ (from 1 above). Exactly 100 cm³ of it contains 0.00600 moles and this has a mass of 0.72 g.
Thus one mole of the acid has a mass of $0.72/0.00600 = 120 \text{ g}$.



7. Information from **2** and **6** should allow the students to identify the acid as benzoic acid ($pK_a = 4.19$, molecular mass = 122.13).

These are only examples of what students can calculate from the information given.

Suggested approach

During trialling the following instructions were given to students and proved to be extremely effective:

1. Working as a group discuss the task and carry it out. You can if you wish divide the work amongst you and then gather the results together.

Such discussion can play a vital part in working out a solution to an open-ended problem where divergent thinking is required. Several minds working on a problem together can stimulate ideas that one on its own could not manage. A few minutes should be spent discussing the task at the start of the exercise, with further discussion as required.

2. Working as a group, prepare a short (ca 5-minute maximum) presentation to give to the rest of the class. If possible all group members should take part: any method of presentation (such as a blackboard, overhead projector, etc) can be used.

Outline the problem, describe what you did and explain your calculations and conclusions but do not give too much detail. After the presentation, be prepared to accept and answer questions and to discuss what you did with the rest of the class.

Background information

To calculate the pH during titration of a weak acid with sodium hydroxide solution.

$$K_a = [H^+][A]/[HA]$$

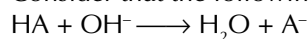
where $[H^+]$, $[A]$ and $[HA]$ are all equilibrium concentrations.

$$[H^+] = K_a \times [HA]/[A] \text{ or } pH = pK_a + \log([A]/[HA])$$

Two methods of calculating the pH are set out below.

Method a

Consider that the following reaction goes to completion



Then $[A] = [OH^-]_{\text{added}}$ (ie $[OH^-]$ in total volume before any reaction)

$$\text{and } [HA] = [\text{acid}]_{\text{total}} - [OH^-]_{\text{added}}$$

eg consider the case where exactly 5 cm³ of 0.100 mol dm⁻³ sodium hydroxide has been added to the 25.00 cm³ of the 0.0600 mol dm⁻³ weak acid.

$$[A^-]_{\text{at equilibrium}} = [OH^-]_{\text{added}} = 5.00 \times 0.100/30.00$$

$$= 0.1667 \text{ mol dm}^{-3}$$

$$[HA]_{\text{at equilibrium}} = [\text{acid}]_{\text{total}} - [OH^-]_{\text{added}}$$



$$\begin{aligned}
 &= [(25 \times 0.00600)/30.00] - 0.01667 \\
 &= 0.0500 - 0.01667 \\
 &= 0.03333 \text{ mol dm}^{-3} \\
 \text{Then pH} &= \text{p}K_a + \log [A^-]/[HA] \\
 &= 4.20 + \log (0.01667/0.03333) \\
 &= 3.90
 \end{aligned}$$

Method b

This more precise method of calculation is not necessary in this case but must be used for dilute solutions, *ie* when $[H^+]$ and/or $[OH^-]$ is/are comparable with $[Na^+]_{\text{added}}$ or $[\text{acid}]_{\text{total}}$.

For electrical neutrality, the concentration of positive charge is equal to the concentration of negative charge in the solution *ie*

$$[H^+] + [Na^+] = [A^-] + [OH^-]$$

$$[A^-] = [H^+] + [Na^+] - [OH^-] \quad \{1\}$$

$$\text{Also } [HA] = [\text{acid}]_{\text{total}} - [A^-] \quad \{2\}$$

eg consider the same case as in method **a** above

$$K_a = [H^+][A^-]/[HA]$$

which, from equations {1} and {2} above, gives

$$K_a = \frac{[H^+] \times ([Na^+] + [H^+] - [OH^-])}{[\text{acid}]_{\text{total}} - ([Na^+] + [H^+] - [OH^-])}$$

$[OH^-]$ can be neglected at this stage in the titration since it is very much less than $[H^+]$ and $[Na^+]$

$$K_a = \frac{[H^+] \times ([Na^+] + [H^+])}{[\text{acid}]_{\text{total}} - ([Na^+] + [H^+])}$$

Rearranging this gives a quadratic equation in $[H^+]$

$$[H^+]^2 + [H^+] \times (K_a + [Na^+]) - K_a \times ([\text{acid}]_{\text{total}} - [Na^+]) = 0$$

Substituting the following:

$$K_a = 6.31 \times 10^{-5}$$

$$[Na^+] = (5.00 \times 0.100)/30.00 = 0.01667 \text{ mol dm}^{-3}$$

$$[\text{acid}]_{\text{total}} = (25.00 \times 0.00600)/30.00 = 0.0500 \text{ mol dm}^{-3}$$

$$\text{gives } [H^+]^2 + 0.0167 \times [H^+] - 2.103 \times 10^{-6} = 0$$

which has one real solution



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$[H^+] = 1.265 \times 10^{-4} \text{ mol dm}^{-3}$, and thus

$\text{pH} = 3.90$ (the same figure as obtained by method **(a)**).



21. On the acid trail

Find out and list as much information as you can – no matter how trivial – about the weak acid from the experimental results below.

A student was given a solution in water of a solid organic compound known to be a weak, monoprotic (monobasic) acid. In order to find out some information about the compound and its solution she titrated a 25.00 cm³ sample against exactly 0.1 mol dm⁻³ sodium hydroxide solution. The following pH titration data were obtained:

Volume (cm ³)	0.00	5.00	8.00	10.00	12.00	14.00	14.50	14.80	15.00	15.20	15.50	16.00
pH		3.90	4.26	4.47	4.80	5.35	5.70	6.07	8.39	10.70	11.90	11.39

The student then carefully evaporated a 100 cm³ sample of the original solution to dryness and obtained a solid of mass 0.72 g.

You should refer to any sources of information that you think might help such as your notebooks, textbooks and data books. Ask for assistance if you get stuck.