E13 VOLUMETRIC ANALYSIS
Acid / base titrations

THE TASK
To use volumetric analysis to determine accurately concentrations in acid / base reactions.

THE SKILLS
By the end of the experiment you should be able to:
• prepare a standard solution,
• weigh by difference,
• perform each of the experimental steps required in an accurate titration,
• perform volumetric analysis calculations.

OTHER OUTCOMES
• You will develop generic scientific skills that include obtaining accurate experimental measurements and their subsequent use to give results with high accuracy and precision.

INTRODUCTION
Volumetric analysis is a technique that employs the measurement of volumes to determine quantitatively the amount of a substance in solution. In any reaction between two or more species, the reaction equation will show the stoichiometric ratio of reacting species. Take, for example, the reaction between solutions of potassium hydroxide and nitric acid. The reaction equations are:

Molecular: HNO₃ + KOH → H₂O + KNO₃

Ionic: H⁺(aq) + OH⁻(aq) → H₂O(l)

In a volumetric analysis, if one of these species is present in known molar concentration, then by taking a fixed volume of one solution and progressively adding the other solution, it is possible to find a point at which complete reaction of the substances has occurred. This is called the equivalence point. The incremental process is called titration and enables the concentration of a solution to be determined from the ratio of reacting volumes, the stoichiometric equation and the one known concentration.

Up to the equivalence point the reacting solution contains excess of one reactant; after the equivalence point the solution contains excess of the other reactant. Some means of observing this switch-over must be available. In acid/base titrations, the change in colour of an indicator is often used to identify the switch-over. The point at which this observed change occurs is called the end point of the reaction and an appropriate indicator is one in which the end point and the equivalence point are as close together as possible.

Not all chemical reactions are suitable for titrations. An appropriate reaction must fulfil several requirements, these being:
• the reaction must be fast, so that the titration can be performed in a convenient time,
• the reaction must essentially go to completion; that is, it must have a large equilibrium constant,
• the reaction must be free from side reactions so that it can be represented by a single equation,
• it must be possible to determine through observation the equivalence point of the reaction.
In this experiment, a series of acid/base titrations is performed, with the aim of becoming familiar with the techniques of titration and the calculations associated with volumetric analysis. Appendix A5 describes the precise techniques involved in titrations and should be read before the practical session. An example titration and the relevant calculations are presented on the following page. The experiment also includes the preparation of a standard solution using the method of weighing by difference, which leads to the highest possible precision and the lowest risk of contamination. Appendix A4 describes this method and should also be read before the practical session.

Here is an example of an experiment in which a potassium hydroxide solution of unknown concentration, but approximately 0.1 M, is titrated against a standard nitric acid solution that is 1.036 M.

Experiment:

1. The standard solution is diluted 10 fold by taking 25.00 mL of the nitric acid in a pipette which has previously been rinsed with 1.036 M nitric acid. The 25.00 mL is transferred to a volumetric flask, previously rinsed with deionised water, and the volume made up to exactly 250.0 mL with deionised water. The concentration of this solution is 0.1036 M.

2. The diluted nitric acid is introduced into a burette, previously rinsed with 0.1036 M nitric acid and the level adjusted to 0.00 mL.

3. 25.00 mL of the potassium hydroxide solution is transferred by pipette to a conical flask, previously rinsed with deionised water. Two drops of methyl-orange indicator are added.

4. The solution is rapidly titrated until the indicator changes colour from yellow to pink. The end point was reached after the addition of approximately 24 mL of acid.

5. A series of accurate titrations is performed until three readings within a range of 0.10 mL (not ±0.10 mL) are obtained. In each case about 20 mL of acid is added rapidly from the burette and the remainder added slowly in progressively decreasing volumes down to single drops. As the end point is neared, shown by a slight change in colour of the indicator, part-drops are detached from the tip of the burette by touching it against the neck of the conical flask and washing down the inside of the flask with deionised water.

6. A series of “titres” were obtained: 22.75, 22.65 & 22.70 mL, giving a mean of 22.70 mL.

Calculations:

The molecular equation for the reaction is $\text{HNO}_3 + \text{KOH} \rightarrow \text{KNO}_3 + \text{H}_2\text{O}$

1000 mL of 0.1036 M HNO$_3$ contains 0.1036 mol of HNO$_3$.

Therefore 22.70 mL of 0.1036 M HNO$_3$ contains $\frac{0.1036 \times 22.70}{1000}$ mol of HNO$_3$.

As 1 mol of nitric acid reacts with 1 mol of potassium hydroxide,

25.00 mL of unknown KOH contains $\frac{0.1036 \times 22.70}{1000}$ mol of KOH.

Therefore 1000 mL of unknown KOH contains $\frac{0.1036 \times 22.70 \times 1000}{25.00} = 0.09407$ mol of KOH.

That is, the concentration of the unknown KOH is 0.09407 M.
The following procedures assume a perfect knowledge of titration as outlined in Appendix 5. Failure to rinse equipment with the appropriate solution [A5(1.1) and A5(1.2)] will cause wildly inaccurate results. Re-read Appendix 5 and continue to refer to it as often as necessary.

SAFETY

Pipettes are easily broken, especially if the pipette filler is used incorrectly. The use of the pipette filler is explained in detail in Appendix A6. Read this appendix carefully and practise the techniques described, then sign the declaration below before proceeding.

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<th>Student Declaration</th>
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<tr>
<td>I have read Appendix A6 and am fully aware of the correct usage of the pipette fillers.</td>
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Sodium hydroxide solutions react with atmospheric carbon dioxide and so have to be regularly standardised with a primary standard. A high purity solid organic acid such as potassium hydrogenphthalate \( \text{KC}_8\text{H}_5\text{O}_4 \) is commonly used for this purpose.

Experiment 1: Standardisation of 0.1 M sodium hydroxide with potassium hydrogenphthalate as a primary standard

(1.1) In a clean, dry 100 mL beaker take about 40 mL of Solution E13A-NaOH unknown (about 1 M). Pipette 25.00 mL of the solution [A5(1.1)] into a 250 mL volumetric flask [A5(1.2)], make up to 250.0 mL with deionised water and swirl / shake / invert for about 2 minutes to mix the solution thoroughly.

Transfer this solution to a 250 mL conical flask [A5(1.1)] and label this solution as E13B. Retain this as your stock of 0.1 M sodium hydroxide for standardisation.

(1.2) Use the method of weighing by difference (see Appendix A4-4 for details) to weigh out accurately about 4 g of potassium hydrogenphthalate from the sample tube E13C into a clean, dry 100 mL beaker. Your mass should be accurate to \( \pm 0.0002 \) g.

Zero the balance. Place the weighing bottle containing the potassium hydrogenphthalate on the balance pan.

\[
\text{Mass of weighing bottle + potassium hydrogenphthalate} = \underline{ } \quad \text{g}
\]

\[
\text{Mass of weighing bottle with potassium hydrogenphthalate (about 4 g) removed} = \underline{ } \quad \text{g}
\]

\[
\text{Mass of potassium hydrogenphthalate weighed out} = \underline{ } \quad \text{g}
\]

Molar mass of potassium hydrogenphthalate = 204.23 g mol\(^{-1}\)

Hence amount of potassium hydrogenphthalate weighed out = \( \underline{ } \) mol
Add about 50 mL of deionised water and stir to dissolve. Transfer the solution to a 250 mL volumetric flask with the aid of the stirrer and plastic funnel), dilute to 250.0 mL with deionised water and mix to homogenise the solution. Transfer to a 250 mL conical flask [A5(1.1)] and label this solution as E13D.

Concentration of solution E13D
(potassium hydrogenphthalate dissolved in 250.0 mL) = \[ M \]

(1.3) Carry out a rapid titration of Solution E13B in the conical flask with Solution E13D in the burette [A5(4)]; 2-3 drops of phenolphthalein should be used as indicator. The behaviour of this indicator is described in A5(5.2).

For 25.00 mL of Solution E13B, the rough volume found was \[ \text{mL} \] of Solution E13D.

Retain the colourless solution in the conical flask and practise observing the end-point, as follows. Add a few mL of Solution E13B until the solution is pink. Then, using the burette, titrate carefully with Solution E13D until the end-point is obtained (only a few mL should be needed). Add more Solution E13B and titrate again with Solution E13D. Repeat this process until you are confident that you can detect the end-point to within one half-drop.

Now complete the procedure of A5(4) by performing a set of 3 accurate titrations.

For 25.00 mL of Solution E13B the precise volumes of Solution E13D were \[ \text{mL} \], \[ \text{mL} \], \[ \text{mL} \].

If the readings are not within a range of 0.10 mL (not ± 0.10 mL), continue titrating until 3 agreeing results are obtained. Take the mean value of your 3 results. If your titrations vary by more than the accepted amount then discuss the possible causes of error with your demonstrator.

For 25.00 mL of Solution E13B the mean volume found was \[ \text{mL} \].

(1.4) Calculations
The molecular equation for the reaction is

\[ \text{KC}_8\text{H}_5\text{O}_4 + \text{NaOH} \rightarrow \text{NaKC}_8\text{H}_4\text{O}_4 + \text{H}_2\text{O} \]

1000 mL of 1.000 M \( \text{KC}_8\text{H}_5\text{O}_4 \) contains 1.000 mol of \( \text{KC}_8\text{H}_5\text{O}_4 \).

\[ \text{mL} \] of \( \text{M} \) \( \text{KC}_8\text{H}_5\text{O}_4 \) contains \[ \text{mol} \] of \( \text{KC}_8\text{H}_5\text{O}_4 \).

Hence 25.00 mL of unknown \( \text{NaOH} \) (E13B) contains \[ \text{mol} \] of \( \text{NaOH} \).

Therefore 1000 mL of \( \text{NaOH} \) (E13B) contains \[ \text{mol} \] of \( \text{NaOH} \).
Concentration of NaOH (E13B) is \[ = \text{M} \]

Therefore the concentration of NaOH (Solution E13A) is \[ = \text{M} \]

Correct result \[ = \text{M} \]  
Demonstrator's Initials

Experiment 2: Titration of acetic acid with standard sodium hydroxide

Determination of the acetic acid content of vinegar

(2.1) Dilute 25.00 mL of Solution E13E-CH₃COOH-unknown (about 0.8 M) to 250.0 mL.

This is now Solution E13F-CH₃COOH-unknown (about \[ = \text{M} \])

(2.2) Use the method of A5(4) to titrate 25.00 mL of Solution E13B-NaOH-\[ = \text{M} \] in the conical flask with Solution E13F in the thoroughly rinsed burette; use phenolphthalein as indicator - A5(5.2).

For 25.00 mL of Solution E13B, the volumes of Solution E13F-CH₃COOH-unknown found were

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<th>Precise volumes</th>
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(2.3) Calculations

The molecular equation for the reaction is \( \text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{NaCH}_3\text{CO}_2 + \text{H}_2\text{O} \)

25.00 mL of \( \underline{M} \) NaOH contains \( \underline{\text{mol}} \) of NaOH.

Hence \( \underline{\text{mL}} \) of diluted vinegar contains \( \underline{\text{mol}} \) of CH\(_3\)COOH.

Therefore 1000 mL of diluted vinegar contains \( \underline{\text{mol}} \) of CH\(_3\)COOH.

Concentration of CH\(_3\)COOH in the diluted vinegar is \( \underline{\text{M}} \) and the concentration of CH\(_3\)COOH in the undiluted vinegar is \( \underline{\text{M}} \).

In 1.000 L of vinegar there is \( \underline{\text{mol}} = \underline{\text{g}} \) of CH\(_3\)COOH.
POST-WORK

Barium hydroxide forms several hydrates. A specimen of barium hydroxide, suspected of being a hydrate, was prepared and analysed as follows to determine its formula.

3.632 g of the compound was dissolved in water to give 250.0 mL of solution. 25.00 mL of this solution was titrated with 0.0987 M HCl, using methyl-orange as indicator. Precise titrations of 23.34, 23.26, and 23.29 mL of HCl were obtained. Determine the formula of the compound.