E13 VOLUMETRIC ANALYSIS
Acid base titrations

Volumetric analysis is a technique which employs the measurement of volumes to quantitatively determine 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 the reaction between solutions of **KOH** and **HNO_3** (see Example 1). The reaction equation is:

$$\mathbf{HNO_3 + KOH \rightarrow KNO_3 + H_2O}$$

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. In order to observe this change, some type of indicator is required, for example by a change in colour. 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 technique of titration, the reaction response and the calculations associated with volumetric analysis (see Example 1).

Appendix 5 of the Laboratory Manual details the techniques used in titrations and should be read before the practical session.

EXAMPLE 1

Here is an example of an experiment in which a **KOH** solution of unknown concentration, but approximately 0.1M, is titrated against a standard **HNO_3** solution which is 1.036M.

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 and two drops of methyl-orange indicator added.

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

5. A series of accurate titrations is performed until three reading within 0.05 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 "titers" is obtained: 22.75, 22.65, 22.70 mL giving a mean reading of 22.70 mL.

Calculations

1. The equation for the reaction is

   $$\mathbf{HNO_3 + KOH \rightarrow KNO_3 + H_2O}$$

2. Moles of nitric acid used is

   (concentration/M) x (volume/L) = (0.1036 mol L^{-1})(22.70 x 10^{-3} L) = 2.352 x 10^{-3} mol

3. As 1 mole of nitric acid reacts with 1 mole of potassium hydroxide, amount of potassium hydroxide = 2.352 x 10^{-3} mol

4. This is from 25.00 mL of solution, so

   $[OH^-]$ = (2.352 x 10^{-3} mol / (25.00 x 10^{-3} L) = 0.9408 M