# CHAPTER 10
# TITRIMETRIC ANALYSIS

## THEORETICAL CONSIDERATIONS

### 10.1 TITRIMETRIC ANALYSIS

The term 'titrimetric analysis' refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called the **standard solution**, see Section 10.3. The weight of the substance to be determined is calculated from the volume of the standard solution used and the chemical equation and relative molecular masses of the reacting compounds.

The term 'volumetric analysis' was formerly used for this form of quantitative determination but it has now been replaced by **titrimetric analysis**. It is considered that the latter expresses the process of titration rather better, and the former is likely to be confused with measurements of volumes, such as those involving gases. In titrimetric analysis the reagent of known concentration is called the **titrant** and the substance being titrated is termed the **titrand**. The alternative name has not been extended to apparatus used in the various operations; so the terms volumetric glassware and volumetric flasks are still common, but it is better to employ the expressions graduated glassware and graduated flasks and these are used throughout this book.

The standard solution is usually added from a long graduated tube called a burette. The process of adding the standard solution until the reaction is just complete is termed a **titration**, and the substance to be determined is **titrated**. The point at which this occurs is called the **equivalence point** or the **theoretical** (or **stoichiometric**) **end point**. The completion of the titration is detected by some physical change, produced by the standard solution itself (e.g. the faint pink colour formed by potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an indicator; alternatively some other physical measurement may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a colour change or the formation of turbidity) in the liquid being titrated. The point at which this occurs is called the **end point of the titration**. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs; this represents the titration error. The indicator and the experimental conditions should be so selected that the difference between the visible end point and the equivalence point is as small as possible.

For use in titrimetric analysis a reaction must fulfil the following conditions.

1. There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.
2. The reaction should be relatively fast. (Most ionic reactions satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of a reaction.
3. There must be an alteration in some physical or chemical property of the solution at the equivalence point.
4. An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction. [If no visible indicator is available, the detection of the equivalence point can often be achieved by following the course of the titration by measuring (*a*) the potential between an indicator electrode and a reference electrode (**potentiometric titration**, see Chapter 15); (*b*) the change in electrical conductivity of the solution (**conductimetric titration**, see Chapter 13); (*c*) the current which passes through the titration cell between an indicator electrode and a depolarised reference electrode at a suitable applied e.m.f. (**amperometric titration**, see Chapter 16); or (*d*) the change in absorbance of the solution (**spectrophotometric titration**, see Section 17.48).]

Titrimetric methods are normally capable of high precision (1 part in 1000) and wherever applicable possess obvious advantages over gravimetric methods. They need simpler apparatus, and are, generally, quickly performed; tedious and difficult separations can often be avoided. The following apparatus is required for titrimetric analysis: (i) calibrated measuring vessels, including burettes, pipettes, and measuring flasks (see Chapter 3); (ii) substances of known purity for the preparation of standard solutions; (iii) a visual indicator or an instrumental method for detecting the completion of the reaction.

## 10.2 CLASSIFICATION OF REACTIONS IN TITRIMETRIC ANALYSIS

The reactions employed in titrimetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation–reduction reactions, involves a change of oxidation state or, expressed another way, a transfer of electrons.

**1. Neutralisation reactions, or acidimetry and alkalimetry.** These include the titration of free bases, or those formed from salts of weak acids by hydrolysis, with a standard acid (**acidimetry**), and the titration of free acids, or those formed by the hydrolysis of salts of weak bases, with a standard base (**alkalimetry**). The reactions involve the combination of hydrogen and hydroxide ions to form water.

Also under this heading must be included titrations in non-aqueous solvents, most of which involve organic compounds.

**2. Complex formation reactions.** These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a soluble, slightly dissociated ion or compound, as in the titration of a solution of a cyanide with silver nitrate

($2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$) or of chloride ion with mercury(II) nitrate solution ($2Cl^- + Hg^{2+} \rightleftharpoons HgCl_2$).

Ethylenediaminetetra-acetic acid, largely as the disodium salt of EDTA, is a very important reagent for complex formation titrations and has become one of the most important reagents used in titrimetric analysis. Equivalence point detection by the use of metal-ion indicators has greatly enhanced its value in titrimetry.

**3. Precipitation reactions.** These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with a solution of a chloride (Section 10.74). No change in oxidation state occurs.

**4. Oxidation–reduction reactions.** Under this heading are included all reactions involving change of oxidation number or transfer of electrons among the reacting substances. The standard solutions are either oxidising or reducing agents. The principal oxidising agents are potassium permanganate, potassium dichromate, cerium(IV) sulphate, iodine, potassium iodate, and potassium bromate. Frequently used reducing agents are iron(II) and tin(II) compounds, sodium thiosulphate, arsenic(III) oxide, mercury(I) nitrate, vanadium(II) chloride or sulphate, chromium(II) chloride or sulphate, and titanium(III) chloride or sulphate.

## 10.3 STANDARD SOLUTIONS

The word 'concentration' is frequently used as a general term referring to a quantity of substance in a defined volume of solution. But for quantitative titrimetric analysis use is made of standard solutions in which the base unit of quantity employed is the mole. This follows the definition given by the International Union of Pure and Applied Chemistry[1] in which:

> 'The mole is the amount of substance which contains as many elementary units as there are atoms in 0.012 kilogram of carbon-12. The elementary unit must be specified and may be an atom, a molecule, an ion, a radical, an electron or other particle or a specified group of such particles.'

As a result standard solutions are now commonly expressed in terms of molar concentrations or molarity ($M$). Such standard solutions are specified in terms of the number of moles of solute dissolved in 1 litre of solution; for any solution,

$$\text{Molarity } (M) = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}}$$

As the term 'mole' refers to an amount of substance with reference to the specified mass of carbon-12, it is possible to express the relative molecular mass (the basis for the mole) for any substance as the additive sum of the relative atomic masses (R.A.M.s) of its component elements, for example:

The relative molecular mass for sulphuric acid, $H_2SO_4$, is calculated from the relative atomic masses as follows:

| Element | R.A.M. |
|---|---|
| Hydrogen | 1.0079 × 2 = 2.0158 |
| Sulphur | 32.06 × 1 = 32.06 |
| Oxygen | 15.9994 × 4 = 63.9986 |
| Relative Molecular Mass | = 98.0744 |

This approach can be used to obtain the R.A.M. of any compound, so that

1 mole of $Hg_2Cl_2$ has a mass of 0.472 09 kg
1 mole of $Na_2CO_3$, $10H_2O$ has a mass of 0.286 141 kg
1 mole of $H_2SO_4$ has a mass of 0.098 074 kg

It follows from this, that a molar solution of sulphuric acid will contain 98.074 grams of sulphuric acid in 1 litre of solution, or 49.037 grams in 500 mL of solution. Similarly, a $0.1M$ solution will contain 9.8074 grams of sulphuric acid in 1 litre of solution, and a $0.01M$ solution will have 0.980 74 gram in the same volume. So that the concentration of any solution can be expressed in terms of the molar concentration so long as the weight of substance in any specified volume is known.

## 10.4 EQUIVALENTS, NORMALITIES AND OXIDATION NUMBERS

Although molar concentrations are now commonly used in determinations of reacting quantities in titrimetric analysis, it has been traditional to employ other concepts involving what are known as ‘equivalent weights’ and ‘normalities’ for this purpose. In neutralisation reactions the equivalent weight/normality concept is relatively straightforward, but for reduction–oxidation titrations it often requires an understanding of what are known as ‘oxidation numbers’ of the substances involved in the redox reaction. Although the modern approach is to discard this form of calculation and quantitation, the authors of this book fully appreciate that there are many scientists who do prefer to use it, and some who claim it has clear advantages over the molar concept. Because of this, a full explanation of this approach to titrimetry is retained as Appendix 17 but all other quantitative aspects in this book are in terms of moles per litre.

## 10.5 PREPARATION OF STANDARD SOLUTIONS

If a reagent is available in the pure state, a solution of definite molar strength is prepared simply by weighing out a mole, or a definite fraction or multiple thereof, dissolving it in an appropriate solvent, usually water, and making up the solution to a known volume. It is not essential to weigh out exactly a mole (or a multiple or sub-multiple thereof); in practice it is more convenient to prepare the solution a *little* more concentrated than is ultimately required, and then to dilute it with distilled water until the desired molar strength is obtained. If $M_1$ is the required molarity, $V_1$ the volume after dilution, $M_2$ the molarity originally obtained, and $V_2$ the original volume taken, $M_1V_1 = M_2V_2$, or $V_1 = M_2V_2/M_1$. The volume of water to be added to the volume $V_2$ is $(V_1 - V_2)$ mL.

The following is a list of some of the substances which can be obtained in a state of high purity and are therefore suitable for the preparation of standard solutions: sodium carbonate, potassium hydrogenphthalate, benzoic acid, sodium tetraborate, sulphamic acid, potassium hydrogeniodate, sodium oxalate, silver, silver nitrate, sodium chloride, potassium chloride, iodine, potassium bromate, potassium iodate, potassium dichromate, lead nitrate and arsenic(III) oxide.

When the reagent is not available in the pure form as in the cases of most alkali hydroxides, some inorganic acids and various deliquescent substances, solutions corresponding approximately to the molar strength required are first prepared. These are then standardised by titration against a solution of a pure substance of known concentration. It is generally best to standardise a solution by a reaction of the same type as that for which the solution is to be employed, and as nearly as possible under identical experimental conditions. The titration error and other errors are thus considerably reduced or are made to cancel out. This indirect method is employed for the preparation of, for instance, solutions of most acids (the constant boiling point mixture of definite composition of hydrochloric acid can be weighed out directly, if desired), sodium hydroxide, potassium hydroxide and barium hydroxide, potassium permanganate, ammonium and potassium thiocyanates, and sodium thiosulphate.

## 10.6 PRIMARY AND SECONDARY STANDARDS

In titrimetry certain chemicals are used frequently in defined concentrations as reference solutions. Such substances are referred to as **primary standards** or **secondary standards**. A primary standard is a compound of sufficient purity from which a standard solution can be prepared by direct weighing of a quantity of it, followed by dilution to give a defined volume of solution. The solution produced is then a primary standard solution. A primary standard should satisfy the following requirements.

1. It must be easy to obtain, to purify, to dry (preferably at 110–120 °C), and to preserve in a pure state. (This requirement is not usually met by hydrated substances, since it is difficult to remove surface moisture completely without effecting partial decomposition.)
2. The substance should be unaltered in air during weighing; this condition implies that it should not be hygroscopic, oxidised by air, or affected by carbon dioxide. The standard should maintain an unchanged composition during storage.
3. The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0.01–0.02 per cent.)
4. It should have a high relative molecular mass so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0.1–0.2 mg; for an accuracy of 1 part in 1000, it is necessary to employ samples weighing at least about 0.2 g.)
5. The substance should be readily soluble under the conditions in which it is employed.
6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below:

(*a*) **Acid-base reactions** — sodium carbonate $Na_2CO_3$, sodium tetraborate $Na_2B_4O_7$, potassium hydrogenphthalate $KH(C_8H_4O_4)$, constant boiling point hydrochloric acid, potassium hydrogeniodate $KH(IO_3)_2$, benzoic acid ($C_6H_5COOH$).
(*b*) **Complex formation reactions** — silver, silver nitrate, sodium chloride, various metals (e.g. spectroscopically pure zinc, magnesium, copper, and manganese) and salts, depending upon the reaction used.
(*c*) **Precipitation reactions** — silver, silver nitrate, sodium chloride, potassium chloride, and potassium bromide (prepared from potassium bromate).
(*d*) **Oxidation–reduction reactions** — potassium dichromate $K_2Cr_2O_7$, potassium bromate $KBrO_3$, potassium iodate $KIO_3$, potassium hydrogeniodate $KH(IO_3)_2$, sodium oxalate $Na_2C_2O_4$, arsenic(III) oxide $As_2O_3$, and pure iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as sodium tetraborate $Na_2B_4O_7, 10H_2O$, and copper sulphate $CuSO_4,5H_2O$, are found by experiment to be satisfactory secondary standards.[2]

A secondary standard is a substance which may be used for standardisations, and whose content of the active substance has been found by comparison against a primary standard. It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against a measured volume of a primary standard solution.

# NEUTRALISATION TITRATIONS

## 10.7 NEUTRALISATION INDICATORS

The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the **equivalence point**, **stoichiometric point**, or **theoretical end point**; the resulting aqueous solution contains the corresponding salt. If both the acid and base are strong electrolytes, the solution at the end-point will be neutral and have a pH of 7 (Section 2.17); but if either the acid or the base is a weak electrolyte, the salt will be hydrolysed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact pH of the solution at the equivalence point can readily be calculated from the ionisation constant of the weak acid or the weak base and the concentration of the solution (see Section 2.19). For any actual titration the correct end-point will be characterised by a definite value of the hydrogen-ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances, called **neutralisation** or **acid–base indicators**, change colour according to the hydrogen-ion concentration of the solution. The