

CHAPTER I

INTRODUCTION

General principles

Methods employed in quantitative chemical analysis may be divided broadly into two main classes, gravimetric and volumetric. In the former, the constituents of a substance are determined by separation and weighed in the form of compounds of known composition. In the latter, the substance to be estimated is allowed to react in solution with another substance of which a solution of known strength has been made; and the volume of the solution of known strength which is required for the completion of the reaction with a certain definite volume of the solution of the substance to be determined is observed. In order that a volumetric determination may be successfully carried out, it is essential that the end of the reaction may be clearly visible to the eye by the appearance or disappearance of some characteristic colour in the solution. Volumetric analysis possesses a great advantage over gravimetric analysis, viz., that the determination of a substance may be carried out with a very much smaller expenditure of time. In a gravimetric method it is necessary to separate the particular constituent which it is desired to determine in a state of great purity; while in a volumetric method such perfect separation is very seldom required, the presence of relatively large quantities of other substances which do not interfere with the particular reaction having in general no effect upon the accuracy of the determination.

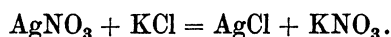
Accuracy of volumetric analysis

The conditions which determine the accuracy of a volumetric method are threefold: firstly the purity of the substance which is employed for making up the solution of definite strength known as the standard solution; secondly the accuracy of the measuring

vessels; and thirdly, the sensitiveness of the change of colour or other device for indicating the completion of the reaction. When these three conditions are fulfilled, volumetric methods will be found to bear favourable comparison with the best gravimetric methods.

Equivalent weights

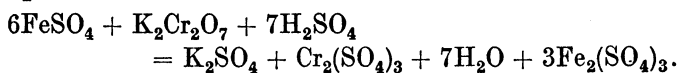
The equivalent weight of a substance is that weight of it which will react with a certain definite weight of some other substance. For example, it is an experimental fact that 169.9 grammes of silver nitrate will completely precipitate the chlorine in 74.56 grammes of potassium chloride by double decomposition according to the equation



Again, if silver nitrate be precipitated by means of hydrochloric acid, it is found that 169.9 grammes of silver nitrate will precipitate the chlorine in 36.47 grammes of hydrogen chloride. These experimental results are expressed by saying that one gramme molecular weight of silver nitrate is equivalent to 74.56 grammes of potassium chloride and to 36.47 grammes of hydrogen chloride respectively.

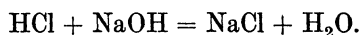
Again, it has been shown by experiment that one gramme molecular weight (40.01 grammes) of sodium hydroxide is capable of neutralizing exactly 49.04 grammes of sulphuric acid, or 36.47 grammes of hydrochloric acid, or 45.01 grammes of anhydrous oxalic acid. In other words, these particular weights of sulphuric, hydrochloric and oxalic acids are said to be chemically equivalent to one gramme molecule of caustic soda and to one another.

If we consider a third type of reaction, viz., the oxidation of a solution of ferrous sulphate in presence of dilute sulphuric acid to ferric sulphate by means of potassium dichromate, accurate experimental work has shown that one gramme atomic weight of iron (metal), or 55.85 grammes, requires 49.03 grammes of potassium dichromate for complete transformation from the ferrous to the ferric condition, the reaction taking place in accordance with the equation

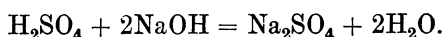


The equivalent weight of potassium dichromate is therefore 49.03 relative to one gramme atomic weight of iron undergoing oxidation from the ferrous to the ferric condition.

It is clear from what has been stated that the equivalent weight of a compound is not necessarily identical with its molecular weight although it is closely related to it. In the case of an element the equivalent weight is equal to the quotient of the atomic weight by the valency. Considering only substances which combine directly with hydrogen, we might define the equivalent of a substance as that weight of it in grammes which will combine with 1.008 grammes of hydrogen. But if we wish to extend our definition in a consistent manner to substances which do not combine directly with hydrogen, we must study the behaviour of such substances towards some other element whose equivalent weight relative to hydrogen is accurately known. For example, it has been shown that 1.008 grammes of hydrogen combine directly with 35.46 grammes of chlorine producing 36.47 grammes of hydrogen chloride. If this gas be now dissolved in water it will be found to neutralize 40.01 grammes of sodium hydroxide according to the equation



Again, the neutralization of sulphuric acid by caustic soda resulting in the formation of sodium sulphate and water takes place according to the equation



From this equation it follows that the equivalent weight of sulphuric acid is half its molecular weight. The double decomposition of hydrochloric acid and silver nitrate resulting in the formation of silver chloride and nitric acid shows that the equivalent of silver nitrate is 169.9.

In the third example which we have been considering, viz., the oxidation of a ferrous salt to the ferric condition by means of potassium dichromate, the value of the equivalent of this oxidizing agent is most easily seen from the fact that its decomposition may be regarded as due to the breaking down of the molecule $\text{K}_2\text{Cr}_2\text{O}_7$ into K_2O , Cr_2O_3 , and three atoms of oxygen, which are effective in the conversion of the iron from the ferrous to the ferric condition.

Now it is an experimental fact that two molecules of hydrogen (four atoms) combine with one molecule (two atoms) of oxygen in the formation of water. Since the atomic weights of hydrogen and oxygen are respectively 1.008 and 16, it is clear that the equivalent of oxygen is 8, or in other words, one atom of oxygen is chemically equivalent to two atoms of hydrogen. Since potassium dichromate contains three atoms of oxygen which are available for the transformation of ferrous into ferric iron, these three atoms of oxygen are equivalent to six atoms of hydrogen. The equivalent weight of potassium dichromate is therefore one-sixth of its molecular weight or $\frac{1}{6}$ of 294.2 grammes or 49.03 grammes.

The three examples which we have discussed will indicate that by the adoption of equivalent weights a perfectly consistent inter-relationship between a large number of substances will be found to exist. We may therefore frame a definition of the term equivalent which will lead to such a relationship in the following terms. The equivalent of any substance, element or compound, is that weight of it in grammes which will either directly or indirectly bring one gramme of hydrogen into chemical action.

The importance of a consistent inter-relationship between the equivalent weights will be more readily apparent later. For the present the rôle of the equivalent in the calculation of results of volumetric determinations will be discussed.

Calculation of results

Suppose that a volume of v_1 cubic centimetres of a substance A is being determined, and that a volume of v_2 cubic centimetres of a substance B containing w grammes per cubic centimetre is required to complete the reaction, the weight x , in grammes, of substance A in each cubic centimetre is determined by the equation

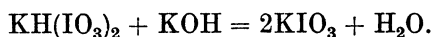
$$\frac{v_1 x}{v_2 w} = \frac{\text{equivalent of } A}{\text{equivalent of } B} \dots\dots\dots(1).$$

Normal solutions

In volumetric analysis a considerable saving of arithmetical work may be effected by the employment of standard solutions which contain the equivalent weight of the substance in grammes dissolved in one litre of the solution. Such standard solutions

are termed normal solutions; or in other words, a normal solution may be defined as a solution of such a strength that one litre of it contains that weight of the solute which is chemically equivalent to one gramme of available hydrogen. For many purposes solutions of normal strength are too strong; in such cases, it is usual to employ solutions of semi-normal or of deci-normal strength, while for certain special work solutions of centi-normal strength are used. Solutions of normal, semi-normal, deci-normal, and centi-normal strength are conveniently abbreviated by the symbols N , $\frac{N}{2}$, $\frac{N}{10}$, $\frac{N}{100}$ respectively. The advantage of employing solutions of normal or of a sub-multiple of normal strength may be seen from the fact that 20 c.c. of a solution of deci-normal HCl will neutralize 20 c.c. of a deci-normal solution of NaOH or will precipitate 20 c.c. of a deci-normal solution of AgNO_3 , in every case without any residue of either reagent remaining unacted on.

The reaction between equal volumes of solutions of normal or of some sub-multiple of normal strength however does not hold good in all cases, as the following example will show. Potassium bi-iodate $\text{KH}(\text{IO}_3)_2$ is a substance which can react either as an acid or as an oxidizing agent. In the former case, one molecule of the substance will neutralize one molecular proportion of potassium hydroxide with formation of two molecules of potassium iodate according to the equation



This reaction indicates that a normal solution of potassium bi-iodate should contain the molecular weight of the substance (390 grammes) dissolved in one litre. In the latter case potassium bi-iodate will liberate iodine from potassium iodide in presence of an acid, one molecule of the bi-iodate liberating six molecules of iodine as represented by the equation



Since one molecule of potassium bi-iodate liberates six molecules of iodine which are equivalent to twelve atoms of hydrogen, it follows that as an oxidizing agent the normal solution of this substance should contain one-twelfth of the molecular weight in grammes per litre.

It is clear, therefore, that the equivalent weight of a volumetric reagent is not an invariable magnitude like the molecular weight, but may be different in different reactions. It is in other words impossible to prepare normal solutions of *all* substances which shall possess the property that a given volume of one shall react quantitatively with an equal volume of any of the others. However, the number of substances which do conform consistently to the normal system is so great that even at the present time the system is of great practical value.

For many technical purposes it is usual to prepare standard solutions of such strength that the number of cubic centimetres of solution required for titration corresponds to a certain percentage of purity of the substance which is being examined.

Classification of methods in volumetric analysis

There are three main methods in volumetric analysis. The first is the direct method which includes all cases where the substance to be determined is estimated as the result of a single decomposition in the solution; such processes include the determination of acids by means of alkalis, of chlorides by silver nitrate, and of ferrous salts by means of potassium dichromate as well as numerous others. Secondly, there are indirect methods in which one or more intermediate reactions come into play; such processes include the determination of peroxides by distilling with hydrochloric acid, passing the chlorine into excess of potassium iodide, and determining the liberated iodine by means of sodium thiosulphate. Lastly, there are methods in which the substance to be determined is treated with a measured excess of some other substance for the purpose of reacting with it, and the excess of the added substance is then determined by some other reagent. As an example of this residual method, reference may be made to the estimation of ammonium salts by adding a known excess of standard alkali, boiling the solution to effect the decomposition of the ammonium salt and the removal of the ammonia, and then determining the excess of alkali remaining over by means of standard acid.

There are no general rules for selecting any one of these three general methods in preference to the others. There are many

substances which may be determined by any of these methods with equally satisfactory results. In certain cases it is convenient to make a combination of the direct or of the indirect method with the residual method.

Besides classifying volumetric methods according to the general experimental procedure, it is convenient to classify them according to the type of reaction which takes place in effecting the estimation. Three main types of chemical action are made use of in most of the commonly occurring volumetric processes. Firstly there is neutralization, or the double decomposition of acids and bases resulting in the formation of a salt and water; this method is employed for the estimation of acids and alkalis. In the second, analysis is effected by oxidation or reduction, the substance being converted from a lower to a higher degree of oxidation by means of an oxidizing agent of known value, or conversely from a higher to a lower degree of oxidation by means of a standard reducing agent. In the third the determination of the substance is effected by precipitation in an insoluble form by double decomposition, as in the determination of silver in solution by potassium chloride.

Classification of volumetric processes according to the main types of reaction which take place is convenient for many purposes, but it does not include all processes. The determination of copper by the decolorization of an ammoniacal solution of the metal by means of potassium cyanide does not admit of classification under any of the foregoing heads.

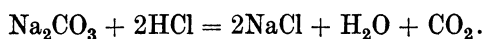
Apparatus employed in volumetric work

It is perhaps superfluous to give an account of the ordinary measuring vessels—pipettes, burettes, and measuring flasks—employed in volumetric analysis, since no written description of them can possibly make the reader as familiar with them as practical work in the laboratory. A few details regarding the use of burettes and pipettes however must be given. These vessels must be thoroughly cleansed before use, and then washed out with a small quantity of the liquid with which they are to be filled in order to prevent dilution of the solutions with water adhering

to the surface of the glass. The correct reading of graduated apparatus is important. In consequence of capillarity, the surface of a liquid in a narrow vessel is always curved; and if, as is usually the case, the liquid wets the glass, the surface will take the form of a concave meniscus. In reading the height of the liquid, the level of the lowest part of the meniscus is always taken, and it is important to place the eye on a level with the meniscus, as otherwise errors will be introduced. In allowing the contents of pipettes to flow into flasks previous to titration, sufficient time must be allowed for the liquid to drain down the walls of the vessel. The same remark may be made in titrating liquids when the liquid is allowed to flow rapidly from the burette; before reading the level of the liquid, time must be given for the liquid to drain down the tube, since otherwise the burette reading will be too high.

Errors in volumetric analysis

It has been already stated that the accuracy of a volumetric process depends on three main factors, viz., the purity of the substance employed for making up the standard solutions, the accuracy of the measuring vessels, and the sensitiveness of the change of colour for indicating the completion of the reaction. Besides these factors there are others which depend upon the conditions of experiment, and in this connexion reference must be made to the influence of the strength of the working solutions upon the accuracy of the process. This may perhaps best be illustrated by a practical example. Suppose it is desired to determine the percentage of sodium carbonate in a specimen of an impure alkaline substance by titration with standard hydrochloric acid. The reaction takes place in accordance with the equation



Is the determination more accurate when carried out with normal acid or with deci-normal acid?

Suppose that 0.5 gramme of the substance is weighed out and titrated with normal acid, and that 4.0 cubic centimetres of acid are required. The weight of anhydrous sodium carbonate is equal to 4×0.053 grammes, and the percentage of it is 42.4.

If in the determination an error of one-tenth of a cubic centimetre in the burette reading is made, that is, if 4.1 c.c. are used instead of 4.0 c.c., the weight of sodium carbonate is 4.1×0.053 grammes, and the percentage of it is 43.4.

If instead of weighing out 0.5 gramme for the determination, 5 grammes are taken and titrated with normal acid, 40 c.c. of acid will be required, corresponding to a weight of 40×0.053 grammes of sodium carbonate, or a percentage of 42.4.

Suppose that in the determination the reading of the burette is 40.1 c.c. instead of 40.0 c.c., the error introduced is only one part in 400, with the result that the percentage of sodium carbonate will be 42.5.

The result of the example which we are discussing is to show the advantage of adjusting matters so that a relatively large volume of liquid is run out from the burette. An error of one-tenth of a cubic centimetre gives rise to a smaller error the greater the volume of the liquid run out.

If we modify the procedure in the above experiment by titrating the alkaline carbonate with deci-normal hydrochloric acid instead of the normal acid, and take 0.5 gramme of the substance, the titration with deci-normal hydrochloric acid will require 40 c.c., corresponding to 40×0.0053 grammes of sodium carbonate, that is to a percentage of 42.4. If an error of 0.1 c.c. is made, that is, if the burette reading is 40.1 c.c. instead of 40.0 c.c., the error in the final result will lead to a percentage of sodium carbonate equal to 42.5, or approximately to an error of one part in four hundred.

It is clear that we have realized the same degree of accuracy by working with deci-normal acid and taking the smaller quantity of substance as we have realized by employing normal acid with ten times the quantity of substance. When economy of material is a consideration, the employment of the more dilute acid is therefore to be recommended.

The advantage of working with a deci-normal standard solution in preference to one of normal strength is however obviously only secured if the change of colour denoting the completion of the reaction, or the end-point as it is called, is defined with equally great precision in dilute solution to what it is in a more concentrated solution. This is by no means always the case; and in the

particular example which has been quoted, where the end point is usually defined by the addition of a drop of methyl orange (Chapter VIII), the change of colour is somewhat more sharply defined in solutions of normal strength than in solutions of decinormal strength. For this reason, it is inadvisable to frame any hard and fast rules for the employment of more dilute rather than of more concentrated standard solutions; all that can be said is that the conditions should be adjusted so that as large a volume of liquid is allowed to flow from the burette as possible; in no case should less than 10 c.c. be run in.

In discussing the accuracy of volumetric determinations, particularly as regards the calculation of results from experiments, it is of course essential to know how much reliance is to be placed upon the measuring vessels. Ordinary pipettes and burettes are usually to be relied upon to an accuracy of the order of one-half per cent. If greater accuracy than this is required it is necessary to calibrate the measuring vessels by filling with water and determining the weight of water which they contain or deliver. If we are dealing with ordinary apparatus which has not been specially calibrated, it is not only mere waste of time to continue the arithmetical work beyond a certain point, but the result has no definite meaning. The process of calculation should be carried only a *little* way beyond the degree of accuracy of the experimental work, in order to ensure that no error is introduced into the final result by the process of calculation.

In connexion with the accuracy of measuring vessels, it is important to bear in mind that the process of weighing out the substance for the standard solution need not be carried out with greater precision than corresponds to the accuracy of the vessels which are to be employed to measure the standard solution. As a matter of fact the process of weighing should be carried out a *little* more accurately than the accuracy of the measuring vessels in order to ensure that the maximum accuracy of the standard solution is realized.

In carrying out volumetric determinations, it is sometimes asked by beginners whether to run the standard solution from the burette into the solution the strength of which is being determined, or to reverse the process, that is, to measure out a known volume