

G. FOWLES

VOLUMETRIC
ANALYSIS



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by

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PREFACE

IN any branch of chemistry where rapid or repeated estimations are required there is little need to point out the merits of volumetric methods of analysis. The simplicity of the apparatus used, the ease of the manipulation involved, the rapidity with which an estimation may be made once a solution is obtained, and the accuracy attainable make volumetric methods suitable both for occasional and routine analysis. The popularity of these methods among technical and academic chemists is a sufficient testimony to their worth.

For the teacher of chemistry, volumetric analysis not only provides a means whereby quantitative results of a satisfactory accuracy can be obtained by large classes, but the exposition of its fundamental principles affords a favourable opportunity of illustrating the application of many points of physical chemistry, such as the common ion effect, the solubility product, the mass action law, adsorption, and the oxidation-reduction potential. The selection of examples illustrative of the principles of physical chemistry from customary analytical processes furthers the study of both subjects; on the one hand, the employment of these principles makes them a real possession and not a memorised phraseology, whilst a volumetric determination arranged to obtain the greatest accuracy becomes an application of these principles and not a mechanical repetition of a set of instructions.

This book presents an elementary survey of volumetric analysis from a theoretical and practical standpoint as applied to the estimation of common metals, acid radicals, and familiar organic compounds, but it does not treat of the bringing into solution of every difficultly soluble substance.

Chapter I deals with the preparation based on first principles of a standard solution of an acid and one of a base. Typical neutralization processes are then treated in detail, the principle

of the determination is explained, the volumetric technique is introduced as required, and the method of calculating the result shown. The limited applicability of certain procedures is pointed out, and the necessity for studying the action employed is illustrated by the investigation of some particular examples. Such a course constitutes the author's method of introducing the study of volumetric analysis to a class preparing for the School Certificate Examination: it may be omitted by advanced students or read for a revision of the elementary conceptions.

Chapter II contains general remarks applicable to all volumetric processes. It consists essentially of a discussion on accuracy, and all the factors which affect it, including the testing and manipulation of apparatus, the selection of substances as standards, and the chemical considerations concerned.

The next four chapters treat of the three great divisions into which volumetric processes may be divided, viz. Acidimetry and Alkalimetry, Oxidation-Reduction methods—for convenience Iodometry is treated separately from the other oxidation-reduction processes—and Precipitation Processes. Each of these divisions is introduced by some exposition of the physico-chemical principles involved, and the salient features of these principles are illustrated by qualitative experiments. It is hoped that in this way the theory may be mastered before the practical work is approached. Thus in Chapter III Neutralization processes introduced in Chapter I are dealt with again, but more thoroughly: the theory of indicators receives considerable attention: the symbol pH is introduced at an early stage because its use simplifies several of the subsequent explanations.

In Chapter IV, which treats of oxidation-reduction processes, an experimental non-mathematical exposition of the conception of the oxidation-reduction potential has been attempted, so that the behaviour of oxidizing and reducing agents may no longer appear bewildering and irregular, but capable of simple explanation, and in many cases able to be predicted. Indeed, throughout the book an endeavour has been made to present chemistry as a series of related phenomena rather than as a collection of isolated facts.

Precipitation processes considered in Chapter VI are prefaced with remarks on the phenomena of adsorption, so frequently met with in analysis, as well as on the solubility product and other relevant matters.

A synopsis, which constitutes the last chapter, contains the volumetric process for the estimation of all common metals, acid radicals, and many organic compounds. Of the estimations not described in the text, the principle and brief outline only of the method are given. The problem of extracting a working procedure from this information should not be beyond the capability of the student who has mastered the main portion of the book. In selecting estimations for this synopsis out of the abundance available an endeavour has been made to include, as far as possible, only those which have been repeatedly reported upon as satisfactory by working chemists, while some well-known methods, such as the iodometric estimation of mercury, the estimation of copper by potassium cyanide, and bismuth as chromate, which have been found unreliable have been omitted.

The march of science has not left volumetric analysis behind; its literature is now considerable, and every year new indicators are announced, new methods devised, and new reactions employed. Criticisms and records of experience of new methods appear together with the thorough investigation of old ones in the light of the modern knowledge of physical chemistry. All this new work is largely in vain if the old, less accurate, and more troublesome methods are still persisted in, and the better ones left buried in the original literature.

In this book an attempt has been made to incorporate the best of the modern work, and some of the traditional methods have either been omitted or given as alternatives. For instance, in neutralization processes standard substances other than sodium carbonate and oxalic acid are recommended, and litmus is replaced by methyl red and other modern synthetic dyes. Diphenylamine is introduced as an internal indicator for many dichromate titrations, and various dyes as adsorption indicators in precipitation processes. Potassium iodate and potassium bromate are included in the oxidimetric reagents,

and in reduction processes attention is called to the use of titanium sulphate in an open burette as suggested by Russell; the preparation and use of liquid amalgams is also described. Of the many rapid yet accurate methods—the product of modern study—included in this book, may be mentioned the estimation of copper by Bruhns, the direct determination of ferric iron by Hahn and Windisch, and the estimation of persulphate by Kurtenacker and Kubina.

The only originality claimed by the author is in the presentation of the elementary principles and the exposition of the various points of theory—the outcome of years of experience in teaching the subject. With regard to the new methods and reagents, the original papers have been consulted in most cases, and the estimations—except some of those in the synopsis—have been repeated. Occasionally a more simple procedure has been given by the omission of some refinement, the worth of which for the extra accuracy claimed and the time expended was doubtful. In making the selection and in the expression of views I have been considerably helped by the records in the chemical journals of the investigations and conclusions of experienced chemists who have given such methods and reagents an extended trial. While the work was in progress the literature of analysis was enriched by three important works. On the theoretical side, *Analytical Processes*, by T. B. Smith, contains a critical examination of analytical processes from the point of view of modern physical chemistry. *Applied Inorganic Analysis*, by (the late) W. F. Hillebrand and G. E. F. Lundell, is the work of the distinguished chemists of the U.S. Bureau of Standards who have performed thousands of estimations and made a life-study of analysis. *Volumetric Analysis*, by Kolthoff and Furman, is an up-to-date critical work suitable for experienced chemists. I have drawn freely on these works and have also consulted *The Study of Indicators and the Law of Mass Action*, by H. Hartley; *The Determination of Hydrogen Ions*, by W. M. Clark; *The Theory and Use of Indicators*, by E. B. R. Prideaux; and *The Theory of Quantitative Analysis* by H. Bassett; and on practical points the works of Treadwell and Hall, Sutton, and Beckurts.

The above volumes are recommended to the student who

requires a deeper knowledge of the subject than is given in this book.

The estimations found herein have not been limited exclusively to those given in the above works, which are written for experienced chemists and deal mostly with technical analyses. The present work is designed for students; I have therefore preferred to insert some methods—such as Rivett's estimation of a sulphate and Kurtenacker's determination of a persulphate (which illustrate the application of some important principle) rather than those whose chief claim is that they are used largely in commercial analyses. When later the student himself improves an old process, devises a new one, or adapts one to the requirements of his own work, it is a grip of the principles which will help him rather than an acquaintance with the details of the current technical process.

The rapid advance of all sections of science makes it increasingly difficult for teachers and students, particularly those pressed for time or remote from libraries, to keep in touch with the modern developments of even one section. Especially is this the case of volumetric analysis, where new developments are dependent on progress in other branches. To such teachers and students it is trusted this book will be helpful: no examination syllabus has been followed in its construction, but the subject-matter should be more than sufficient for university students, for candidates for University Scholarships, for the Higher School Certificate, and for the National Certificate in Chemistry. It is hoped that the method of presenting the subject may provide suggestions for teachers who have not yet evolved methods of their own, and that the directions are sufficiently explicit, and the explanations sufficiently clear for the private student to carry on alone or with only occasional help from a demonstrator.

In conclusion I should like to thank my colleagues, Messrs G. J. Francis, E. D. Goddard, and F. Jackson, for criticism and help on various points, and D. C. M'Intyre, A.R.C.A., for the preparation of the coloured frontispiece.

I gladly acknowledge my indebtedness to E. J. Bowen, M.A., Fellow and Tutor of University College, Oxford, for reading and criticizing the theoretical matter of Chapters III-VI, and

for the help he so generously gave me in the preparation of a simple account of the oxidation-reduction potential.

It is difficult adequately to express what I owe to my colleague, W. Wheatley, M.A., who has not only prepared the diagrams but has read through the whole of the typescript—in many places, following his suggestion, the phrasing has been altered in the interest of clarity and correctness.

G. F.

January 1932

PREFACE TO REVISED EDITION

THE quarter of a century which has passed since the first edition was written has seen the introduction into volumetric analysis of numerous indicators and organic reagents but of no new method for the presentation of its fundamental principles. Except for rewriting an occasional explanatory section, with the idea of making its meaning clearer, I have therefore left the framework of the original text unaltered. Thus, I have recast the sections on pH and on redox indicators, and in addition to extending the material I have offered a new theoretical approach to Jamieson's ICl reaction. The Synopsis, revised and extended, now becomes Chapter IX.

At the request of teachers, a collection of numerical problems, with answers, and a table of logarithms have been added. As an introduction to this section I have further attempted to show students the way to understand and master any volumetric calculation. A chapter on ceric sulphate as an oxidant, and a supplement giving further notes on the subject-matter of the body of the book, are also new to this edition. This arrangement has permitted the introduction of valuable additional matter, such as Hoppner's indicator for carbonate and the technique of Willard and Furman for the precipitation of calcium oxalate, without unduly disturbing the text. Novelties, however, little tried out by experienced analysts, and whose chemistry is not typical (such as the determination of potassium by sodium tetraphenyl boron), have not been included.

Our expanding knowledge of the electronic theory of valency has introduced into volumetric analysis a new class of reagents—complexing compounds—of immeasurable potentiality. It is simpler and more rapid to deprive a solution of an ion by 'complexing' rather than by precipitation. Electronic theory reveals the molecular structures which have complexing ability, and shows how this quality may be intensified. It has thus indicated the possibility of the synthesis of an untold number of organic complexing agents. During recent years the preparation and application of many of these compounds by Schwarzenbach and

his school has promised to revolutionize certain sections of analytical practice. Accordingly I have added a new chapter (VII) on *Complexing Processes* corresponding to Chapter VI on *Precipitation Processes*. This new chapter includes a simple exposition of the chemistry of a complex system, so that the student may have a general understanding of any such reaction he is using. Among the determinations therein described is one using the most outstanding of these newer complexing agents—ethylenediamine tetracetic acid.

My grateful thanks are due to friends and industrial concerns for help with this revision.

British Drug Houses Ltd, of Poole, Dorset, gave me trial samples of Solochrome Black and other modern indicators of their preparation, and the Geigy Company Ltd, of Manchester, supplied me with Sequestrol (EDTA) and its salts, and with the literature of volumetric procedures evolved in their own laboratories.

Help afforded me by a succession of former pupils calls up warm recollections of strenuous school days filled with chemical activity. Awaiting the taking-up of their University Scholarships or other positions, A. G. Maddock, R. E. Goddard, D. Ramsay, J. W. Cook, H. H. Topper, and H. P. Luckeuck, with youthful enthusiasm, love of accuracy, and keen eyesight, eagerly investigated new volumetric procedures and studied the behaviour of recently-introduced indicators, some of which they had themselves prepared. Later, as university or industrial chemists, they supplied me with ideas for improving their school textbook.

Many of the numerical problems were collected for me and the answers worked out by B. J. Moody of Bristol Grammar School, and I am further indebted to him for some valuable suggestions.

With especial pleasure I acknowledge my debt to Charles Holt of Harrow Weald County Grammar School, who was associated with me in editing S.M.B. Chemistry III. He not only read and polished the manuscript, but he keenly reviewed the new material in the light of his wide experience of chemistry teaching.

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G. F.

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CHAPTER I

INTRODUCTION TO VOLUMETRIC ANALYSIS

THERE are several methods by which the amount of a substance—such as an element or radical—in a compound or mixture may be determined. A gaseous constituent may be liberated and its volume measured—the Gasometric method. The colour which a definite amount of the substance gives with a reagent may be compared with a standard tint—the Colorimetric method. A definite compound of the substance may be isolated and weighed—the Gravimetric method; or a reaction in solution may be measured—the Volumetric process. Some methods depend on the separation of a metal, *e.g.* arsenic by reduction, or upon the electrolytic deposition of a metal, in other methods a physical property is measured, such as the density, or the lowering of the freezing-point of a solution. Most of these processes are of limited application; the gravimetric and volumetric processes are of general application, and of these the volumetric process is the more rapid.

In gravimetric analysis all the measurements are made by weighing. The element or radical to be estimated is converted into a compound of known composition. This compound is separated from the other constituents of the substance, purified, dried, and weighed. Thus the silver in an alloy could be converted into silver chloride: this compound contains 75.4 per cent. of silver, hence if a definite amount of the alloy yielded 1 gm. of silver chloride, the weight of alloy taken must contain .754 gm. of silver.

The volumetric estimation of a substance occupies less time than the corresponding gravimetric estimation, because in

volumetric analysis such processes as the drying of precipitates are not necessary, and the determination can often be made without actual separation of the radical concerned. Advantage is taken of the rapidity with which many chemical actions take place in solution, and of the fact that the dissolved substances react in equivalent proportions. A definite amount of the substance (A) to be analysed is made into a solution. A substance (B) which will rapidly and quantitatively react with substance A is likewise made into a solution—containing a definite number of equivalents of B per given volume. The solution of B contained in a measuring vessel is gradually run into solution A until the reaction between A and B is complete. The volumes of the two solutions which have been used must have contained equivalent amounts of A and B. From the volume of solution B used and a knowledge of the chemical action which has taken place the amount of radical in the substance being analysed can be calculated. Suppose that it is desired to find the amount of silver present in an alloy of silver and copper. For the second liquid a solution of hydrochloric acid containing 3.65 gm. of HCl per litre could be used. If a solution of a weighed amount of the alloy required just 100 c.c. of the hydrochloric acid solution—that is, a volume containing .355 gm. of chloride—to precipitate the whole of the silver as silver chloride, then the solution of the alloy must contain 1.08 gm. of silver, for .355 gm. of chlorine and 1.08 gm. of silver are chemically equivalent quantities.

The process of running a solution from a burette into the solution being analysed until equivalent quantities of the solutes are present is called a *titration*.

A standard solution (p. 3) is usually placed in the burette and the solution being analysed is then said to be titrated with or against this standard solution.

It is necessary to be able to detect with accuracy the stage when the two solutions are present in equivalent amounts—the Equivalence Point or End Point of the titration. For this purpose a third substance is often added, which, by some visible effect, such as a change of colour or by the formation

of a precipitate, reveals the end point. Such substances are called *indicators*.

Chemical actions suitable for volumetric analysis have not yet been found for all substances: thus there is no satisfactory method for the estimation of silicon and no highly accurate volumetric process for the determination of potassium or of the perchlorate radical. In many cases the volumetric determination of a substance is equally as accurate as the correspondent gravimetric one and sometimes superior to it, as in the determination of nitrates, borates, and ammonia. The volumetric estimation is always to be preferred where rapidity is required or where many repetitions of the same kind of estimation are needed.

This book deals mostly with the actual volumetric processes employed, and only occasionally mentions the methods of bringing difficultly soluble substances into solution: for information of this nature the student should consult larger works such as, *Standard Methods of Chemical Analysis*, Scott; *Analytical Chemistry*, vol. ii, Treadwell and Hall; *Applied Inorganic Analysis*, Hillebrand and Lundell.

It is obvious that for volumetric analysis there will be required:

1. Apparatus for the accurate measurement of volumes.
2. Stocks of solutions of known strength.
3. Above all a knowledge of the chemical processes involved in the analyses.

Standard Solutions

A *Standard Solution* is one whose strength is known.

By *strength* is meant the grams of dissolved substance (or of its reactive constituent) per litre of solution.

The strength is usually expressed in equivalents of the reactive constituent per litre of solution.

A standard solution is always made by dissolving the standard substance in a small volume of the solvent and then diluting to the required volume: never by the unsound method of dissolving the weighed substance in the definite

volume of solvent. Thus if 10 gm. of salt are dissolved in 40 c.c. of water and the solution diluted to 100 c.c. and thoroughly mixed, then 10 c.c. of this solution will contain 1 gm. of salt. But if 10 gm. of salt are dissolved in 100 c.c. of water the volume of the solution formed is not 100 c.c. but about 103 c.c., and 10 c.c. of this solution will contain less than 1 gm. of salt.

Standard solutions are usually made of such a strength as to simplify the work and allow the results to be readily calculated. The chemical equivalent of the reagent (or of its reactive constituent) in grams per litre is chosen as the unit, and a solution of this strength is called a *Normal Solution*.

The number of equivalents in a litre of solution is often called the *Normality* or *Titre* of the solution. Thus a solution containing one-tenth of an equivalent per litre would be a solution one-tenth normal—written $\frac{N}{10}$ or 0.1 N.

Probably the simplest reaction in solution which lends itself to volumetric measurement is the neutralization of an acid by a base. We shall begin with this reaction and learn how to prepare the standard solutions of acid and base required for the experiment.

Preparation of a Normal Acid Solution

Acids are compounds of hydrogen and an acid radical, and it is the presence of the hydrogen which imparts to an acid those characteristic properties which we call 'acidic.' This hydrogen of an acid—hydrogen united to an acid radical—we shall call 'acidic hydrogen.' Some acids, for instance, oxalic acid, contain water of crystallization; the hydrogen of this water is not, of course, acidic hydrogen: also, of the four atoms of hydrogen in a molecule of acetic acid only one possesses acidic properties.

A *Normal Acid Solution* must contain 1 gm. of acidic hydrogen per litre.

As seen from the knowledge stored up in the formulæ

$$\text{HCl} = 36.5, \text{HNO}_3 = 63, \frac{\text{H}_2\text{SO}_4}{2} = 49,$$

36.5 gm. of hydrochloric acid, 63 gm. of nitric acid, and 49 gm. of sulphuric acid will each provide 1 gm. of acidic hydrogen. But we cannot obtain these quantities by weighing out the required amount of the so-called pure acids of the laboratory, for they are all mixtures of the pure acid with water. Concentrated hydrochloric acid contains about 37 per cent. of HCl, concentrated nitric acid about 66 per cent. of HNO_3 , and 'pure sulphuric acid' about 95-98 per cent. of H_2SO_4 .

Of these acids the most suitable for the preparation of a normal solution is hydrogen chloride, for not only is it easily obtained in a pure state but its composition is known, for it is a feature of most courses of chemistry to show that 1 gm. of hydrogen unites with 35.5 gm. of chlorine to form 36.5 gm. of hydrogen chloride.

Procedure—100 c.c. will be a convenient volume of solution to prepare, and this should contain 3.65 gm. of HCl. We therefore place a little water in a 100-c.c. measuring flask and, after weighing, pass in dry gaseous hydrogen chloride until 3.65 gm. have dissolved, then dilute the contents to 100 c.c. Fix up an apparatus such as that shown in Fig. 1, slide six or seven pieces of rock salt of the size of small nuts into the preparation flask (A): the wash bottle (B) should contain a little concentrated sulphuric acid to indicate the rate at which the gas is passing. Before beginning, about one-third fill the graduated flask (C) with water, insert the delivery pipette (D),

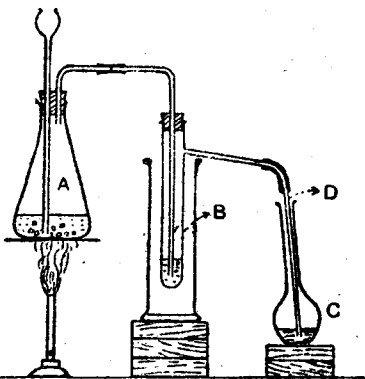


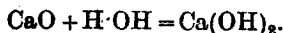
FIG. 1.—Preparation of a standard solution of HCl.

and weigh. Cover the salt with strong sulphuric acid, and by warming with a small flame get a fast steady stream of hydrogen chloride. Occasionally detach the graduated flask (C)—including the delivery tube—and rapidly weigh it to see how fast the gas is being dissolved. Continue passing in the acid until the weight shows that just over 3.65 gm. have dissolved. Now lift the delivery pipette just clear of the liquid and rinse any acid solution adhering to it into the flask (C). Next calculate what volume of solution the weight of dissolved HCl should be in to be at the rate of 36.5 gm. per litre: for instance, suppose 3.725 gm. have been dissolved, then this amount should be in 102 c.c. of solution. Dilute the contents of the flask to the graduation mark, add the extra 2 c.c. of water from a burette, and make the contents of the flask homogeneous. To do this, hold the flask in one hand, insert the stopper, or close the flask with a finger, invert the flask and rock it with the other hand. Repeat the inversion and rocking two or three times; in this way any heavy layer at the bottom becomes thoroughly mixed with the rest of the solution. Store the solution in a bottle which has previously been washed and dried, and label it HCl 1.0 N. Medicine bottles are useful for this purpose, they are of a suitable size, pack together easily, and are readily obtainable.

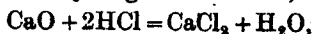
Preparation of a Normal Solution of a Base (Alkali) *

A normal solution of a base contains the equivalent weight in gm. per litre, so that a given volume will exactly neutralize an equal volume of normal acid solution.

Most bases are metallic hydroxides, that is, metallic oxides combined with water,



We may consider that it is the oxygen of the metallic oxide which neutralizes the hydrogen of an acid,



and we shall call this oxygen 'basic oxygen.'

* For a note on the terms base and alkali, see p. 69.