QUANTITATIVE CHEMICAL ANALYSIS

BY

ALEX. CHARLES CUMMING, D.Sc.

AND

SYDNEY ALEXANDER KAY, D.Sc.

FORMERLY LECTURERS IN CHEMISTRY IN THE UNIVERSITY OF EDINBURGH

NINTH EDITION REVISED BY

FRANCIS CLINT GUTHRIE, M.A., F.I.C., AND
JOHN TRENGOVE NANCE, M.A.

LECTURERS IN CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL

EXTRACT FROM PREFACE TO FIRST EDITION

THIS book is intended primarily for University and College students. We have endeavoured to arrange the book in such a manner that some knowledge of the principles of Quantitative Analysis may be acquired by a practical study of the subjects included in Parts I., II., and III., and that the further requirements of those who are making a special study of Chemistry should be met by the later portions of the book.

Most of the typical exercises in Parts II. and III. may be performed with pure substances, but it is desirable that the student should be accustomed from the commencement of his course to the analysis of substances of " unknown " composition. The serious student finds that this enhances the value of the exercise, whilst the occasional student who " only wants to know the method " has his attention directed to the real purpose of Quantitative Analysis. A list of solutions suitable for analysis is given in the Appendix. In describing typical exercises, care has been taken to give the practical details of manipulation as fully as possible, and where full details are not given, reference is invariably made to the pages where they may be found.

In Part V., all the common elements and radicals are considered, together with the methods for their separation and determination. As the arrangement is alphabetical and copious references to other parts of the book are given, it is hoped that this section will prove a useful index.

In order to avoid constant repetition of particulars in regard to the concentration of reagents, it has been assumed throughout the book that, unless the contrary is stated, the concentration of a reagent is that specified in the Appendix. The concentrations usually recommended for indicator solutions are such that even

" a few drops " is often more than ought to be used. The concentrations recommended in the Appendix are so chosen that 1 c.c. of the indicator is the normal amount required, and throughout the book it is assumed that these dilute indicator solutions are used.

All the diagrams have been specially drawn for the book—in a large number of cases from original photographs of the apparatus.

CHEMISTRY DEPARTMENT
UNIVERSITY OF EDINBURGH
October 1913

PREFACE TO NINTH EDITION

ALTHOUGH no new sections have been added to the present edition, a considerable number of smaller additions and alterations have been made. Amongst these may be mentioned the gravimetric determination of cobalt as phosphate, and the well-known volumetric estimation of nickel by the cyanide method. The separation of iron from zinc in one operation by ammonium hydroxide, and a somewhat similar separation of iron from manganese under controlled pH conditions are described. An alternative method is given for the separation of strontium from calcium, depending on the solubility of calcium nitrate in anhydrous acetone, in which strontium nitrate is practically insoluble. The determination of barium by direct titration with sodium carbonate using phenolphthalein as indicator has been modified, and the method as now described is applicable also to the determination of strontium and of calcium.

The list of solutions for analysis given in the Appendix has been increased, and a table for the specific gravity of acetic acid for various concentrations is included in this section. It has been suggested that dates should be given of the latest editions of the reference books mentioned in the Appendix, but the revisers consider that this would be inadvisable in view of the publication of subsequent editions of any of these works.

As stated in the previous edition, much of the data for the measurement of volumes and the standardisation of instruments is taken from the pamphlet *Tests on Volumetric Glassware*, issued by the National Physical Laboratory, Middlesex, and is reproduced by the courtesy of the Director.

For the methods given for the determination of tungsten

(p. 389), molybdenum (p. 390), vanadium (p. 273), and chromium (p. 119) in steel, the revisers are indebted to the United Steel Companies Ltd., these being based on standard methods in use in their laboratories, and published in the revised edition of their *Standard Methods of Analysis*.

DEPARTMENT OF INORGANIC AND
   PHYSICAL CHEMISTRY
   UNIVERSITY OF LIVERPOOL
        1945

CONTENTS

PART I.—GENERAL PRINCIPLES

PART II.—VOLUMETRIC ANALYSIS

xi

PART II.—VOLUMETRIC ANALYSIS—*continued*

PART III.—GRAVIMETRIC ANALYSIS

PART IV.—COLORIMETRIC METHODS

PART V.—SYSTEMATIC QUANTITATIVE ANALYSIS

PART V.—SYSTEMATIC QUANTITATIVE ANALYSIS—*continued*

PART VI.—THE ANALYSIS OF SIMPLE ORES AND ALLOYS

PART VII.—GAS ANALYSIS

PART VIII.—WATER ANALYSIS

APPENDIX

QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL PRINCIPLES

WHEN the examination of any substance is undertaken for the purpose of determining the respective amounts of any of its constituents, the investigation is known as **quantitative analysis.** The problem may be a simple or a complex one, depending on the nature of the substance, and on whether a complete or only a partial analysis is required. For many purposes it is not necessary to ascertain the amounts of all the constituents of a substance ; it may be of importance to determine the amount of only one of them. It is comparatively simple to determine, for example, the amount of iron in an ore, the amount of carbon dioxide in a sample of air, or the amount of chloride in a water-supply. On the other hand, it may be necessary to make a complete analysis of a complex ore or rock containing as many as ten or twenty constituents, or to carry out a detailed investigation of a sample of water. The complexity of an analysis depends, however, as much on the nature of the constituents as on their number, and the determination of the amount of even a single constituent may involve a lengthy and refined investigation, demanding the highest skill on the part of the chemist.

Different methods are usually available for the determination of one and the same constituent, but not all of those methods may be applicable to every substance containing it. The choice of the best method often requires careful consideration.

The gravimetric method of analysis usually involves (1) the separation of the constituents of the substance in the form of

insoluble compounds of known composition ; (2) the deter-
mination of the weight of the compounds so obtained.

The volumetric method of analysis, on the other hand, is
based on the use of a reagent of known concentration, and on
the measurement of the volume of this reagent required to
complete the chemical change involved.

A fundamental distinction between the two methods is that
in gravimetric analysis the constituent that is to be determined
must be separated from all the other constituents of the
substance ; whereas, *in volumetric analysis*, the separation of
the constituents is very frequently unnecessary, and one or
more of the constituents of a substance can often be rapidly
and accurately determined in presence of all the others, thus
enormously simplifying the analytical process.

Most substances can be determined either gravimetrically
or volumetrically. In the systematic treatment of the subject
it is convenient to consider gravimetric and volumetric methods
separately ; but in practice the two methods of procedure are
frequently combined, in order that the analysis may be com-
pleted as rapidly and as accurately as possible. When a
complete analysis of a complex substance has to be made, the
constituents must, as a rule, be separated from one another
before the amount of each can be ascertained, and gravimetric
methods are usually employed ; whereas, if only a partial
analysis is required, involving, it may be, only one of the
constituents, volumetric methods are often applicable. The
latter are almost invariably more expeditious than gravimetric
methods, and in analysis for technical purposes where economy
of time is often imperative, volumetric methods—not necessarily
less accurate than gravimetric—are used as far as possible.

As an example in illustration of some of the foregoing
principles, two methods of determining the respective amounts
of iron and aluminium in a solution containing ferric and
aluminium chlorides may be briefly outlined.

(1) In order to accomplish this by gravimetric methods
alone, *the iron and aluminium must be separated* by adding
an excess of sodium hydroxide to a weighed or measured
portion of the solution. The *precipitate*, which consists of
ferric hydroxide, is filtered ; the *filtrate* contains the aluminium
as sodium aluminate.

The *precipitate*, which is contaminated with alkali hydroxide,

is dissolved in dilute acid, and ammonia is added in order to reprecipitate the ferric hydroxide. The latter, after filtration, is converted into ferric oxide which is weighed.

The *filtrate*, containing the sodium aluminate, is acidified with hydrochloric acid, and the aluminium is precipitated as aluminium hydroxide by adding ammonia. The precipitate is filtered and, by heating to a high temperature, is converted into alumina which is weighed.

From the weights of ferric oxide and alumina, the respective amounts of iron and aluminium in the solution can then be calculated.

(2) By a combination of gravimetric and volumetric methods, which in this case is much to be preferred, *no separation of the iron and aluminium is necessary*; the procedure is accordingly simpler and more expeditious, and accurate results are more readily obtained.

The iron and aluminium are precipitated together as hydroxides by adding ammonium chloride and ammonia to a weighed or measured portion of the solution, and the precipitate, by heating strongly, is converted into a mixture of ferric oxide and alumina which is weighed. The mixture of ferric oxide and alumina is then dissolved (or another measured portion of the original solution is taken), and the iron in the solution is determined volumetrically. The volumetric process consists, briefly, in reducing the ferric salt to the ferrous state by means of some suitable reducing agent, and in then determining the amount of iron present by means of a solution of potassium permanganate of known concentration. The aluminium does not interfere with the volumetric determination of the iron.

It is then easy to calculate how much ferric oxide is present in the mixture of ferric oxide and alumina, and the difference between the total weight of the mixed oxides (which has already been determined gravimetrically) and the weight of the ferric oxide is the weight of the alumina. The respective amounts of iron and aluminium in the original solution can then be calculated.

The Balance

For accurate analytical work, a suitable balance, capable of supporting a maximum load of 100 to 200 grams in each pan, is indispensable. It is important that the maximum load, whatever it may be, should never be exceeded. With a good balance, properly adjusted and used, very accurate measurements can be made. For example, it is possible to distinguish between two masses of about 10 grams each when they differ in weight by only 0·1 milligram, *i.e.* by 1 part in 100,000. A balance is, therefore, a delicate instrument of precision, and the greatest possible care must be taken in using it. *The rules regarding the use of the balance* (p. 11) *must be carefully read and thereafter strictly adhered to.*

When weighing in a comparatively rough fashion, it is generally assumed that equipoise is established when the excursions of the pointer towards either side of the mid-point of the scale are of equal amplitude. For the following reasons, however, this method is not invariably adopted in accurate work.

(1) The zero-point, or resting-point of the unloaded balance, *i.e.* the position which the pointer would apparently take up if the oscillating beam were allowed to come to rest, seldom coincides exactly with the mid-point of the scale.

(2) Since the oscillating beam, if left to itself, ultimately comes to rest, the amplitude of each oscillation, even when equipoise is established, is *less* than that of the preceding one. It follows that, if an excursion of the pointer to the left is equal to the preceding one to the right, the weight on the right is greater than that on the left (assuming the zero-point to coincide with the mid-point of the scale).

Routine Method of Weighing

In making a weighing, accurate to 0·1 milligram (0·0001 gram), the following method should be used :—

(1) Find the *zero-point* of the balance.

Release the beam carefully, and if necessary set it oscillating so that the pointer moves through about five scale divisions on

either side of the middle point. If it does not oscillate sufficiently, on releasing the beam, this may be brought about by gently opening the balance-case, and wafting air down on to one of the pans and closing the case again. A more satisfactory method is to fit a glass tube through the left-hand side of the balance-case, with one end slightly turned up under the left pan. A rubber bulb is connected to the other end of the tube outside the balance-case. A slight puff of air is sufficient to start the beam swinging, and to increase or decrease the amplitude. Neglecting the first complete oscillation (two excursions of the pointer), carefully observe and note down the next *three* extreme positions of the pointer, two observations being made on one side and one on the other side of the mid-point of the scale. Assume the scale to be numbered from the extreme left towards the right, *e.g.* from 0 to 20, the mid-point being 10, and estimate tenths of the scale divisions.

If, for example, the observations were

Left.	Right.
(1) 5·0	
	(2) 15·8
(3) 5·4	

the turning-point on the left, corresponding to the point 15·8 on the right, is the mean of 5·0 and 5·4, *i.e.* 5·2, and the resting-point is therefore

$$\frac{5\cdot2 + 15\cdot8}{2} = 10\cdot5$$

Repeat the observations several times. The results should not differ by more than one or two tenths of a scale division, and the mean is taken as the zero-point of the balance. As the zero-point is frequently subject to slight fluctuations, it should be determined before each set of weighings is commenced.

(2) Place the vessel to be weighed on the *left* pan of the balance and proceed to counterpoise it. It is best to begin with a weight that will probably prove too heavy, as this may save time in the end. For example, if the weight of the vessel is thought to lie between 15 and 20 grams, the latter weight is placed on the right scale-pan. If, on releasing the beam, the 20-gram weight is seen to be too much, it is replaced by a

10-gram weight, and the necessary smaller weights are added *in regular succession* until the sum of the weights on the right-hand pan is within 0·01 gram less than the weight of the object : *e.g.* if 16·46 grams is too little and 16·47 grams is too much, the smaller weight is left on the pan.

In place of the inconveniently small milligram weights, it is preferable, at this stage, to use a rider, which weighs 0·01 gram, though its effective weight depends on its position on the divided beam. After some experience it will be found possible approximately to estimate, by observing the rapidity of the movement, what additional weight is required to establish equilibrium. If, for instance, it has been found that with 16·46 grams on the pan the pointer is deflected slowly to the right whilst with 16·47 grams it is deflected much more rapidly to the left, the weight of the vessel is nearer 16·46 than 16·47 grams.

Now close the balance-case, and place the rider on the beam in such a position that equipoise is nearly established—for example, at division 3. The beam should be arrested before changing the position of the rider, though after some experience slight alterations may be made while the beam is swinging. Record three oscillations of the pointer, and determine the resting-point. Suppose it is found to be 9·6.

(3) Find the " sensitiveness " of the balance, *i.e.* the displacement of the resting-point produced by an alteration of 1 milligram :—Alter the position of the rider by an amount corresponding to 1 milligram—in such a direction that the resting-point is shifted to the other side of the zero-point—and again determine the resting-point. Suppose it to be 11·1 when the rider is at division 2. The sensitiveness is then equal to

$$11·1 — 9·6 = 1·5 \text{ scale divisions.}$$

(4) Now calculate, as follows, the alteration of the weight necessary to counterpoise the vessel exactly :—

The zero-point—using the figures assumed in the foregoing—is 10·5, and the resting-point with a load of 16·462 grams is 11·1. The vessel weighs, therefore, more than 16·462 grams, the additional amount being equal to that necessary to displace the resting-point from 11·1 to 10·5, or 0·6 of a scale division. Since, however, 1·5 scale divisions correspond to