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QUANTITATIVE ANALYSIS

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赠送书

SECOND EDITION

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PREFACE TO SECOND EDITION

In arrangement and general content, the Second Edition of this book shows no changes from the First Edition. A large portion of the material has been rewritten, however, in order to make those adjustments which laboratory and class use have shown to be desirable.

The following may be noted as among the more important items in the revision. A chapter on the preparation of the sample for analysis has been added to Part I. In the chapter on volumetric methods a new section on common techniques gives complete directions for those operations which are needed in every volumetric determination. The sections on stoichiometry have been expanded to include additional illustrative examples. Dimensional units are introduced into the stoichiometric calculations. The questions and problems have been rewritten, and many new ones have been added. The section on neutralization theory is expanded. Use of indicator blanks in acidimetry is stressed both in theory and practice. In the laboratory exercises on acidimetry, emphasis is placed upon the use of carbonate-free base, with potassium acid phthalate as the recommended primary standard. The sections on oxidation-reduction theory have been completely rewritten, with the conventions changed to make the sign of the oxidation potential conform to general usage among analytical chemists. Redox indicators are discussed, and methods for the selection of a suitable indicator are illustrated by numerical computations. In practically all the laboratory procedures some modification has been made, to eliminate sources of student errors.

We wish to express thanks for the many helpful criticisms and suggestions supplied by users of the first edition, and we hope that errors and omissions in this edition will be called to our attention.

Grateful acknowledgment is made to Dr. G. E. F. Lundell and Dr. J. I. Hoffman for their permission to use the tables of acid-base indicators and of oxidation potentials from *Outlines of Methods of Chemical Analysis*, and to Professor G. Frederick Smith and the editor of *Industrial and Engineering Chemistry* for permission to reproduce the titration curves of Fig. 33.

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PREFACE TO FIRST EDITION

Numerous objectives are sought in teaching quantitative analysis. Aside from becoming familiar with the more common analytical procedures and their applications, the student should also develop a certain degree of technical skill. Moreover, he should understand the theoretical principles upon which the analytical methods are based, and should be able to perform with facility the stoichiometric calculations involved in an analysis. Finally, the well-trained analyst should have a knowledge of the precision and accuracy to be expected of each determination, and he should be aware of the errors which may be encountered. The authors have attempted to correlate these various objectives in the development of this book, and to emphasize all aspects of the subject in connection with each determination. At the same time an effort has been made to keep the presentation as simple as possible.

The book is designed for use in a first-year course in quantitative analysis, and it contains all the material usually treated in a year's work. In the arrangement, however, the needs of the one-semester course have been kept in mind, and the material which is not treated in the first semester's work has been segregated in separate chapters. A logical and continuous development has been sought to facilitate the presentation in the beginning course. Each topic is introduced by a brief description of the methods to be used and a simplified explanation of the theory involved. This is followed by a presentation of the stoichiometry of the method and, finally, by the laboratory procedures. Advanced theory, when given, follows the laboratory procedures.

The book is divided into sections, in order to permit flexibility in teaching. Part I deals with fundamentals, the preparation of equipment, and the use of the analytical balance. After this section is completed the teacher may proceed either with volumetric analysis, in Part II, or with gravimetric analysis, in Part III. Each of these sections is independent of the other, and may be studied as a unit.

Throughout the book, the procedures are set apart from the discussion of methods and of theory. Each procedure is followed by a section of explanatory notes which serves both to clarify the correlation of theory and practice and to emphasize the need for special precautions. It is expected that the student will carefully study the procedure and notes before beginning an experiment. During the analysis he then needs to

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follow only the procedure, which is stated concisely and without embellishment. Details of laboratory technique are repeatedly stressed in the explanatory notes, even at the risk of tiresome repetition, since it is the experience of most teachers that these details cannot be overemphasized. A list of general errors is given in the preliminary discussion of each type of analysis, and in addition each procedure is followed by a list of the specific errors that may be encountered.

A detailed discussion is given for each type of stoichiometric calculation used in analysis. This discussion is illustrated by complete solutions for typical problems, and in addition there are provided numerous problems for home work. Many of these problems illustrate laboratory methods which space limitations have prevented including in the textual material. In connection with the problems for home work a large number of review questions are also given. Most of the questions are designed to emphasize and illustrate points which are treated in the text, but some of them require independent thinking or consultation of more advanced works. Answers have been provided for a portion of the problems, in order to enable the student to assure himself that he is using correct methods of attack, but they are not given for all problems since this may easily lead to the practice of working for an answer.

In the stoichiometry of volumetric analysis, the concept of the milliequivalent is widely used, in consistency with the use of the milliliter as the laboratory unit of volume. In the experience of the authors, the use of the milliequivalent instead of the equivalent facilitates the ability of the average student to grasp the intricacies of stoichiometric calculations.

In the chapters devoted to an advanced treatment of theory a mature level is adopted. There is assumed a thorough knowledge of chemical equilibrium, such as is usually treated in qualitative analysis. Elementary physical chemistry is freely introduced in the section on the theory of oxidation-reduction processes. Much of the theoretical material is developed by the problem method of presentation. Each new point is illustrated by the complete solution of a typical problem, and in addition there are given numerous problems for home work.

A chapter in the first section of the book is devoted to a discussion of precision, errors, and significant figures. The authors feel that these concepts should be introduced early in the course, and that they should be constantly emphasized in connection with all laboratory work. Throughout the earlier determinations the student is encouraged to examine the probable sources of error and to determine for himself the accuracy which may be expected from his results. In addition he is taught to examine his results from the viewpoint of precision.

The section on analysis of a limestone rock gives, in addition to pro-

cedures for a proximate analysis, other methods of general applicability in mineral analysis. Sufficient detail is provided to enable the student to analyze most of the simpler silicate or carbonate rocks.

The last section of the book deals with specialized methods of analysis and with the use of chemical literature. Obviously, an introductory textbook cannot describe many special methods of analysis. In addition to conventional exercises in electrodeposition, the authors have selected for discussion colorimetric methods and potentiometric titrations. These are included because of their growing importance in biological analyses, and are illustrated with procedures which may be included in a first course if desired. It is felt that the section on the use of chemical literature is an important item in training analytical chemists, since the student, at the conclusion of a year's work, should be able to locate and use any method which is published. The authors recommend and use the widespread practice of assigning to each student one analysis for which the original literature must be consulted.

Sections on mathematical operations and on hydrolysis are given in the Appendix. The former is included for the benefit of those students who are inadequately prepared; the latter section is offered as an advanced treatment of complex equilibria for the benefit of superior students.

The selection of student exercises for an elementary textbook is a difficult task because of the great divergence among the practices of various teachers. Therefore every general method is illustrated by procedures for several different analyses. This permits each teacher to choose the preferred type of unknown sample. The authors strongly recommend the use of synthetic solutions as unknown samples for the earlier volumetric analyses, because this type of unknown permits the teacher to give each student an individual sample of accurately known analysis. An objection to this practice is that it does not provide training in the technique of bringing samples into solution, but this training is acquired later in connection with more difficult analyses. In every place that directions are given for the analysis of a prepared solution directions are also given for the analysis of a commercial product or ore.

The authors favor the widely used procedure of teaching volumetric analysis first because this permits the student to become acquainted with the analytical balance by means of the relatively inexact weighings necessary for calibration of volumetric apparatus, and because most of the technique of volumetric analysis is more readily acquired than the exacting technique of gravimetric analysis. If this plan is followed students may be assigned the material of Chapters I, II, III, V, VI, VII

in order. If it is desired to begin with gravimetric analysis, the material of Chapters I, II, III, XV, XVI, XVII constitutes a logical sequence.

The writers desire to acknowledge their indebtedness to Professors W. A. Noyes, Jr., T. F. Young, and W. E. Vaughan for many features of the course upon which much of the book is based. Many useful problems and laboratory hints were furnished by Professors P. C. Gaines, L. O. Hill, and O. E. Sheppard. To the various students who assisted in the preparation of the manuscript and in testing procedures, the authors give their thanks, in particular, to Messrs. A. A. Danish, N. H. Koenig, A. H. Jaffey, D. P. MacMillan, and W. W. Marshall. Professor G. Frederick Smith has kindly read the completed manuscript and has given many valuable criticisms. The standard reference works and textbooks in the field have been freely consulted. Particular acknowledgment should be made to *Applied Inorganic Analysis*, by Hillebrand and Lundell, and to the various works of I. M. Kolthoff and his collaborators.

W. C. Pierce
E. L. Haenisch

Chicago, Illinois
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CONTENTS

LABORATORY EXERCISES

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CHAPTER I

INTRODUCTION

Analytical chemistry, which deals with the determination of the composition of matter, is an important branch of chemical science. Indeed, it may be said to be the basis of all chemistry. The reactions of the elements and their compounds, the facts and theories of organic chemistry, and the fundamental laws of physical chemistry have all been studied by analytical methods. Analytical chemistry, however, is not of importance if considered as a distinct and separate branch of the science; it is of value only in so far as it contributes to the advancement of knowledge or to practical application of the science.

Modern analytical chemistry is subdivided, for convenience of study, into several classes. The more important of these are inorganic qualitative and quantitative analysis, and organic qualitative and quantitative analysis. Identification of the elements in inorganic substances (qualitative analysis) usually precedes quantitative analysis, which has as its objective the determination of the amount of one or more elements present in a sample. Quantitative organic analysis likewise deals with determination of the elementary composition, whereas qualitative organic analysis deals with the identification of organic compounds rather than the identification of the elements present.

The methods of quantitative analysis are classified according to the type of technique employed. The most widely used methods are known as *gravimetric* and *volumetric* analysis. Gravimetric analysis is based upon the *weight* of precipitate obtained from a sample; volumetric analysis is based upon the *volume* of reagent required for reaction with a sample. The difference between the two types of method may be illustrated by an example which utilizes reactions often encountered in qualitative analysis. Chloride ion may be determined by either a gravimetric or a volumetric method. In the gravimetric method a weighed sample is dissolved and treated with silver nitrate in excess. Silver chloride precipitates and is separated by filtration, dried, and weighed. From the weight of precipitate and the weight of sample the percentage of chlorine in the sample may readily be calculated. In the volumetric method a weighed sample is dissolved and a silver nitrate solution of known concentration is slowly added. An *indicator*, in the form of a dye which has been

added to the solution, shows by a color change when the amount of silver ion added is chemically equivalent to the amount of chloride ion in the weighed sample. The weight of chloride ion in the sample can be calculated from the volume and concentration of the silver nitrate solution.

In addition to the methods of gravimetric and volumetric analysis, a large number of more specialized methods are in widespread use. In fact, practically every physical property of matter is made the basis for some type of analysis. Some of the special methods will be considered in Chapters XX, XXI, and XXII.

In all quantitative analyses it is necessary to remove the sought constituent from other substances which might interfere with the determination, or to be assured of the absence of interfering substances. It is, therefore, necessary to have a knowledge of the *qualitative* composition of the sample. Usually it is not necessary to make a complete qualitative analysis before undertaking the quantitative analysis of a sample, but specific tests for certain interfering substances of probable occurrence are often made.

The methods of qualitative analysis are not in general the methods used for the same constituents in quantitative analysis. In qualitative analysis it is sufficient to obtain, in an end test, enough of a constituent for its identification. In quantitative analysis it is usually necessary to make all separations *complete*. Careful workmanship and skilled technique are, therefore, of even more importance in quantitative than in qualitative analysis.

In beginning a course in quantitative analysis it is well to consider the objectives which will be sought. The primary object is to master the use of tools which will be employed throughout all subsequent work in chemistry. Mastery of the tools includes more than acquiring a manual ability to use analytical instruments properly; a well-trained analyst should know this, of course, but in addition he should thoroughly understand the principles upon which the analytical methods are based, and the calculations needed in all types of analysis. Moreover, he should be cognizant of errors which can occur in his determinations and their effects on the results. Further, the analyst should be familiar with the more common types of technique encountered in analyses. Finally, he should have a knowledge of how to use that vast storehouse of information, the chemical literature. No one book or library of books can contain details of all known analytical methods, but the trained analyst can quickly locate, in a good library, any analytical method which has ever appeared in print. The objectives of the beginning courses are, then, the following: (1) to gain skill in the use of analytical equipment, (2) to gain an understanding of the basic theory and of the methods of calculation, (3) to

obtain experience in the use of the more common analytical techniques, and (4) to become acquainted with analytical literature and its use.

In attaining the above objectives there must be a careful selection of material. Obviously it is impossible to study the analytical methods employed for all the known elements, nor would such a procedure be desirable. Attention is centered instead on the *methods* used in analysis, because a few basic methods suffice for all analyses. The basic methods are illustrated by procedures for the analysis of those elements whose determination is most frequently encountered. In this textbook the methods of gravimetric and volumetric analysis are treated in detail. Only a few of the more important special methods are discussed, because after the basic methods are mastered the self-reliant chemist can quickly study and apply special methods without the aid of a teacher.

The arrangement of this book is based upon the methods studied. Part I provides a description of the general equipment used and directions for handling it. This section includes instructions for the use of the analytical balance, the fundamental tool of all analytical methods. Part II is devoted to representative types of volumetric analyses, and Part III to typical gravimetric determinations. Part IV contains a brief description of some special analytical methods which are widely employed and an introduction to the use of analytical literature.

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