QUANTITATIVE ANALYTICAL CHEMISTRY

fourth edition

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PREFACE

A new edition of any textbook gives the authors an opportunity to add new material to keep the book current. At the same time, subject matter that has become of limited value can be condensed or eliminated. But apart from keeping the text material up-to-date, we think that a new edition ought to be a definite improvement over the previous book. Explanations should be made more clear and logical; difficult concepts should be made more understandable. These principles have been our guide in preparing this fourth edition. Above all, we have tried to produce a book that is modern in outlook and covers the material in a manner that is clear and easy to understand.

Part I in particular has been carefully gone over. Many changes have been made, although the general format remains unchanged except for addition of a new chapter (Chapter 10) on acid-base titrations in nonaqueous solvents. Chapter 5 on spectrophotometry has been completely rewritten to include more examples, a modern treatment of all instrumental components, and a discussion of approaches to spectrophotometric determinations. Some marginal topics have been eliminated from Chapter 7 and the treatment of chemical equilibrium has been made clearer and contains more worked-out examples. Chapters 8 and 9 have been reorganized and contain a unique new treatment of acid-base titration curves that is more logical and easier to understand than the usual presentations. Chapter 11 on precipitate-formation titrations has been shortened somewhat from the previous edition. Chapter 12 on complexes and complex-formation titrations has been rewritten; the discussion of equilibrium constants is easier to follow and includes numerous worked examples.

The first fourteen chapters provide the fundamentals for a short course in quantitative analytical chemistry. However, a sound, modern course or course sequence should certainly include at least some of the topics covered in the later chapters of Part I. In this edition, Chapter 16 on electrochemistry has been reorganized and has a new and clearer treatment of polarography. A new section on gas-sensing electrodes has been added to Chapter 17. Reflecting the ever growing importance of chromatography in practical analysis, our coverage of chromatography in Chapters 19–22 remains unusually strong. All of these chapters have been revised and updated, and Chapter 20 on gas chromatography has been completely rewritten.

Spectrophotometry continues to grow in usefulness as a method for quantitative analysis. In Chapter 23, the theory of fluorescence methods has been revised and a section on infrared instrumentation has been added. New sections on inductively coupled plasma in emission spectroscopy and on flameless atomic absorption have been added to Chapter 24. To complete the revisions in Part I, new examples of actual analytical problems have been incorporated into Chapter 25.

Several changes have been made in Part II. A new experiment, Experiment 15 on determining Vitamin C in dehydrated juice solids, has been added. In addition, theoretical material on choosing sample size in Chapter 28 has been moved to Chapter 2; new material on handling a student sample has been substituted for the former. An appropriate form for reporting the gravimetric chloride has been included in Chapter 26 to guide students who do a gravimetric experiment as their first experiment. Finally, we have included only directions for weighing on a single-pan balance, in recognition of the universal use of single-pan balances.

There are many new questions and problems at the end of the chapters in Part I. In almost every case, these are grouped under various headings to provide more convenient selection for assignments or self-study. Answers to approximately half the numerical problems are given in the back of the book. An answer book with worked-out solutions to problems is available for instructors.

The authors wish to thank Robert L. Grob, Larry G. Hargis, Bruno Jaselkis, and John E. Roberts, who read and commented on the manuscript, and Dennis Johnson for his valuable comments on the electrochemistry chapters. We are also grateful to our graduate students and associates who contributed data for figures and assisted us in other ways. Finally, we wish to acknowledge the excellent editorial assistance of David Dahlbacka.

James S. Fritz
George H. Schenk

FORMULA WEIGHTS

(Arranged alphabetically according to atomic symbol. All weights rounded to relative uncertainties between 0.2 and 0.02 ppt.)

$AgBr$	187.78
$AgCl$	143.32
AgI	234.77
$AgNO_3$	169.88
$Al(C_9H_6NO)_3$ (aluminum oxinate)	459.46
Al_2O_3	101.96
As_2O_3	197.84
As_2O_5	229.84
$BaCl_2$	208.25
$BaCl_2 \cdot 2H_2O$	244.27
$BaCO_3$	197.35
$BaCrO_4$	253.33
BaO	153.34
$BaSO_4$	233.40
$CHCl_3$	119.38
CO_2	44.011
$C_2H_4(OH)_2$ (ethylene glycol)	62.07
C_4H_9OOH (*t*-butyl hydroperoxide)	90.13
C_6H_5Br (bromobenzene)	157.02
$CaCO_3$	100.09
CaC_2O_4	128.10
$CaMg(CO_3)_2$	184.41
CaO	56.08
$Ca(OH)_2$	74.10
$CaSO_4$	136.14
$Ca_3(PO_4)_2$	310.18
$Ce_2(C_2O_4)_3$	544.47
CeF_3	197.12
Cr_2O_3	152.00
CuO	79.54
CuS	95.60
$CuSO_4 \cdot 5H_2O$	249.68
FeO	71.85
FeS	87.91
$FeSO_4 \cdot C_2H_4(NH_3)_2SO_4 \cdot 4H_2O$	382.18
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	392.15
FeS_2	119.97
Fe_2O_3	159.69
Fe_3O_4	231.54
$2Fe_2O_3 \cdot 3H_2O$	337.38
HCO_2CH_3 (acetic acid)	60.05
$HCO_2C_6H_5$ (benzoic acid)	122.12
$HCdC_{10}H_{15}O_7N_2$	388.66

HCl	36.46
HIO_4 (periodic acid)	191.91
HNO_3	63.02
HSO_3NH_2 (sulfamic acid)	97.09
$H_2C_2O_4$ (oxalic acid)	90.04
$H_2C_2O_4 \cdot 2H_2O$ (oxalic acid)	126.07
H_2S	34.08
H_2SO_3	82.08
H_2SO_4	98.08
H_3PO_4	98.00
H_5IO_6 (periodic acid)	227.94
HfO_2	210.49
$HgCl_2$	271.50
HgO	216.59
Hg_2Cl_2	472.13
KBr	119.01
$KBrO_3$	167.01
KCl	74.56
$KClO_4$	138.55
$KHC_2O_4 \cdot H_2C_2O_4$	218.16
$KHC_8H_4O_4$ (KHP)	204.23
KI	166.01
KIO_3	214.00
$KIO_3 \cdot HIO_3$	389.93
$KMnO_4$	158.04
KOH	56.11
KSCN	97.18
K_2CrO_4	194.20
$K_2Cr_2O_7$	294.19
K_2O	94.20
K_2SO_4	174.27
$La_2(C_2O_4)_3$	541.89
$MgCl_2$	95.22
$MgCO_3$	84.32
$MgNH_4PO_4$	137.32
MgO	40.31
$Mg_2P_2O_7$	222.57
MnO_2	86.94
MoO_3	143.94
$NH_2CO_2NH_2$ (urea)	60.05
$NH_2(C_4H_9O_3)$ (THAM)	121.14
$NH_2(C_5H_4N)$ (4-aminopyridine)	94.11
NH_3	17.031
NH_4Cl	53.49
NH_4OH	35.05
$(NH_4)_2C_2O_4$	124.10
$(NH_4)_2Ce(NO_3)_6$	548.23
$(NH_4)_2SO_4$	132.14
$NaAl(SiO_3)_2$	202.14
NaBr	102.90
$Na(CH_3CO_2)$ (sodium acetate)	82.04
$Na(C_6H_5CO_2)$ (sodium benzoate)	144.10
NaCl	58.44
NaF	41.99
$NaHCO_3$	84.01
NaH_2PO_4	119.98
NaOH	40.00
Na_2CO_3	105.99
$Na_2C_2O_4$	134.00
$Na_2H_2Y \cdot 2H_2O$ (EDTA)	372.24
Na_2O	61.98
Na_2SO_4	142.04
$Na_2S_2O_3 \cdot 5H_2O$	248.19
$Ni(C_4H_7O_2N_2)_2$ (Ni-DMG$_2$)	288.94
P_2O_5	141.95
$PbCl_2$	278.10
$PbCrO_4$	323.19
PbO_2	239.19
$PbSO_4$	303.25
Pb_3O_4	685.57
SO_2	64.06
SO_3	80.06
SiO_2	60.09
$SnCl_2$	189.61
SnO_2	150.69
$SrCO_3$	147.63
$SrSO_4$	183.68
ThO_2	264.04
TiO_2	79.90
$UO_2(C_{16}H_{13}AsN_2O_5)$	388.16
U_3O_8	842.09
V_2O_5	181.88
Y_2O_3	225.81
Yb_2O_3	394.08
ZnO	81.37
ZrO_2	123.22

CONTENTS

PART I · PRINCIPLES AND THEORY

CHAPTER 1 · INTRODUCTION

1-1. THE NATURE OF ANALYTICAL CHEMISTRY

What Is Analytical Chemistry? Analytical chemistry is the branch of chemistry dealing with the separation and analysis of chemical substances. Traditionally, analysis has been concerned largely with chemical *composition*, but it is coming more and more to include the determination of chemical *structure* and the measurement of physical properties. Analytical chemistry includes both qualitative and quantitative analysis. Qualitative analysis is concerned with *what* is present, quantitative analysis with *how much*. This book deals almost entirely with quantitative analysis. However, it might be appropriate to comment briefly on the qualitative methods used to identify the substances present in a chemical mixture.

The systematic hydrogen sulfide qualitative scheme is helpful in learning and organizing some chemical reactions, but it is no longer used widely as a practical analytical method. The emission spectrograph (see Chapter 24) is a rapid and useful way of detecting the elements present in inorganic samples. Sensitive, selective chemical spot tests have been worked out to detect many ions and molecules. Chromatography is an extremely valuable method of separating and detecting both organic and inorganic substances (see Chapters 19–22). For example, paper and thin-layer chromatography have been used to rapidly identify subgroups in blood [1] and by police laboratories to identify the many inks used in ballpoint pens. Infrared spectra serve as excellent "fingerprints" for identifying organic and many inorganic compounds (see Chapter 23). These, together with other ingenious methods, are the techniques of modern qualitative analysis.

Courses in quantitative analysis traditionally have dealt almost exclusively with the analysis of inorganic material. Nevertheless, analytical chemistry properly includes the analysis of organic material too. Analytical chemistry finds extensive application in the analysis of organic compounds, pharmaceuticals, biochemicals, body fluids, hair, the atmosphere, polluted water, foods, soils, and in many other areas.

[1] "Scientific Methods of Crime Investigation," *Chemistry, 43*, 12 (1969).

What Is an Analytical Chemist? A true analyst, or analytical chemist, has several characteristics. He or she has a knowledge of the methods and instruments used for analysis. He understands the principles of analysis, so that he can apply and, if necessary, modify analytical methods to solve a particular problem; frequently he is a research chemist who studies the theory of analytical processes or develops completely new methods of analysis. He can evaluate and interpret the results of a quantitative analysis.

Above all, an analytical chemist is a problem solver. It has been said that if you can state a problem clearly, it can be solved. An analytical chemist must do just this. By asking questions and gathering information, he or she determines what the actual problem *is*, then uses experience and cleverness to map out a scheme for solving it.

Thus, an analytical chemist is a skilled, well-trained chemist—in sharp contrast with the more numerous technicians or "determinators," who simply twist the dials of an instrument or follow "cookbook" analytical procedures.

What Information Does Chemical Analysis Provide? *Qualitative analysis* may be used to indicate the presence or absence of certain elements, ions, or molecules. For example, the first step in "screening" a suspicious solid sample for lysergic acid diethylamide (LSD) is to examine it under ultraviolet light [1]. Most hallucinogens such as LSD show up as fluorescent or discolored areas that can then be dissolved and tested further. A *structural determination* may be used to define the entire structure of a new drug or to verify only the structure or stereochemistry of a certain part of a newly synthesized molecule.

The most important aspect of analysis is still *quantitative analysis*, with which this book is mainly concerned. A quantitative analysis provides data regarding the chemical composition of matter. These data may be quite detailed, or they may be incomplete and general. The types of quantitative analysis may be classified as follows:

Complete Analysis. The amount of each constituent of the sample is determined quantitatively. For example, a complete analysis of a gasoline sample would tell the percentage of each compound present (hydrocarbons, tetraethyllead, tricresyl phosphate, etc.). In many samples, such an analysis would be a waste of time; instead a "complete" analysis is run for a select number of species. For example, in clinical laboratories, a "complete" blood analysis may involve the determination of eight or twelve species: glucose, Na^+, K^+, bilirubin, alkaline phosphates, etc. [2].

Ultimate Analysis. The amount of each element in a sample is determined without regard to the actual compounds or ions present. An ultimate analysis of a gasoline sample would tell the percentage of carbon, hydrogen, oxygen, lead, phosphorus, etc.

Partial Analysis. The amount of a certain selected constituent in a sample is determined. A partial analysis of gasoline might tell the percentage of tetraethyl-

[2] L. T. Skeggs, *Anal. Chem.*, *38*, 31A (May, 1966).