

**TREATISE
ON
ANALYTICAL
CHEMISTRY**

**PART I
THEORY AND PRACTICE**

VOLUME 2

TREATISE ON ANALYTICAL CHEMISTRY

Edited by I. M. KOLTHOFF

School of Chemistry, University of Minnesota

and PHILIP J. ELVING

Department of Chemistry, University of Michigan

with the assistance of ERNEST B. SANDELL

School of Chemistry, University of Minnesota

PART ~~X~~
THEORY ~~AND~~ PRACTICE
VOLUME 2

INTERSCIENCE PUBLISHERS, NEW YORK-LONDON

Copyright © 1961 by
INTERSCIENCE PUBLISHERS, INC.

ALL RIGHTS RESERVED

LIBRARY OF CONGRESS CATALOG CARD NUMBER 59-12439

Distributed by
Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y.

For Great Britain and Northern Ireland:
Interscience Publishers Ltd., 88/90 Chancery Lane, London, W. C. 2

PRINTED IN U. S. A. BY MACK PRINTING CO., EASTON, PA.

Preface to the Treatise

The aims and objectives of this Treatise are to present a concise, critical, comprehensive, and systematic, but not exhaustive, treatment of all aspects of classical and modern analytical chemistry. The Treatise is designed to be a valuable source of information to all analytical chemists, to stimulate fundamental research in pure and applied analytical chemistry, and to illustrate the close relationship between academic and industrial analytical chemistry.

The general level sought in the Treatise is such that, while it may be profitably read by the chemist with the background equivalent to a bachelor's degree, it will at the same time be a guide to the advanced and experienced chemist—be he in industry or university—in the solution of his problems in analytical chemistry, whether of a routine or of a research character.

The progress and development of analytical chemistry during most of the first half of this century has generally been satisfactorily covered in modern textbooks and monographs. However, during the last fifteen or twenty years, there has been a tremendous expansion of analytical chemistry. Many new nuclear, subatomic, atomic, and molecular properties have been discovered, several of which have already found analytical application. In the development of techniques for measuring these and also the more classical properties, the revolutionary progress in the field of instrumentation has played a tremendous role.

It has been difficult, if not impossible, for anyone to digest this expansion of analytical chemistry. One of the objectives of the present Treatise is not only to describe these new properties, their measurement, and their analytical applicability, but also to classify them within the framework of the older classifications of analytical chemistry.

Theory and practice of analytical chemistry are closely interwoven. In solving an analytical chemical problem, a thorough understanding of the theory of analytical chemistry and of the fundamentals of its techniques, combined with a knowledge of and practical experience with chemical and physical methods, is essential. The Treatise as a whole is intended to be a unified, critical, and stimulating treatment of the theory of analytical chemistry, of our knowledge of analytically useful properties, of the theoretical and practical fundamentals of the techniques for their measurement, and of the ways in which they are applied to solving specific analytical problems. To achieve this purpose, the Treatise is divided into three parts: I, analytical chemistry and its methods; II, analytical chemistry of the elements; and III, the analytical chemistry of industrial materials.

Each chapter in Part I of the Treatise illustrates how analytical chemistry draws on the fundamentals of chemistry as well as on those of other sciences; it stresses for its particular topic the fundamental theoretical basis insofar as it affects the analytical approach, the methodology and practical fundamentals used both for the development of analytical methods and for their implementation for analytical service, and the critical factors in their application to both organic and inorganic materials. In general, the practical discussion is confined to fundamentals and to the analytical interpretation of the results obtained. Obviously then, the Treatise does not intend to take the place of the great number of existing and exhaustive monographs on specific subjects, but its intent is to serve as an introduction and guide to the efficient utilization of these specialized monographs. The emphasis is on the analytical significance of properties and of their measurement. In order to accomplish the above aims, the editors have invited authors who are not only recognized experts for the particular topics, but who are also personally acquainted with and vitally interested in the analytical applications. Only in this way can the Treatise attain the analytical flavor which is one of its principal objectives.

Part II is intended to be very specific and to review critically the analytical chemistry of the elements. Each chapter, written by experts in the field, contains, in addition to a critical and concise treatment of its subject, critically selected procedures for the determination of the element in its various forms. The same critical treatment is contemplated for Part III. Enough information is presented to enable the analyst both to analyze and to evaluate a product.

The response in connection with the preparation of the Treatise from all colleagues has been most enthusiastic and gratifying to the editors. It is obvious that it would have been impossible to accomplish the aims and objectives cited in this preface without the wholehearted cooperation of the large number of distinguished authors whose work appears in this and future volumes of the Treatise. To them and to our many friends who have encouraged us we express our sincere appreciation and gratitude. In particular, considering that the Treatise aims to cover all of the aspects of analytical chemistry, the editors have found it desirable to solicit the advice of some colleagues in the preparation of certain sections of the various parts of the Treatise. They would like at this time to acknowledge their indebtedness to Professor Ernest B. Sandell of the University of Minnesota for his interest and active cooperation in the organizing and in the detailed planning of the Treatise.

Minneapolis, Minn.
Ann Arbor, Mich.

I. M. KOLTHOFF
P. J. ELVING

PART I. THEORY AND PRACTICE

CONTENTS — VOLUME 2

SECTION B. Application of Chemical Principles to Analytical Chemistry (*continued*)

20. Reactive Groups as Reagents: Introduction and Organic Applications. By <i>Leo Schubert and Irving May</i>	811
I. Introduction.....	811
A. Functions of Chemical Reagents.....	811
B. Critical Factors of Reagents.....	812
1. Selectivity and Specificity.....	812
2. Sensitivity.....	813
3. Masking and Unmasking.....	814
4. Addition Agents.....	815
5. Solvent and Solubility.....	815
C. Classification of Reactions.....	816
1. Precipitation.....	816
2. Volatilization.....	817
3. Extraction.....	817
4. Ion Exchange.....	818
5. Chromatography.....	819
6. Complex Formation.....	820
7. Oxidation-Reduction.....	820
8. Formation of Colored Species.....	821
9. Transformation of Organic Compounds into Those with Chromo- phoric or Other Functional Groups.....	821
II. Reagents in Organic Analysis.....	822
A. General Aspects.....	822
B. Objectives of Reagent Applications.....	827
C. Types of Analytical Reactions.....	829
1. Colorimetric Methods.....	829
2. Titrimetric Methods.....	829
3. Gravimetric Methods.....	830
4. Redox Reagents.....	830
5. Manometric Methods.....	831
References.....	831
21. Reactive Groups as Reagents: Inorganic Applications. By <i>Irving May and Leo Schubert</i>	833
I. Inorganic Reagents.....	834
A. Reagents for Group Separations.....	834
1. The Cations.....	834
2. The Anions.....	838
B. Common Oxidizing-Reducing Agents.....	838
C. Common Complexing Agents.....	841
D. Reagents for Extraction and Volatilization.....	843
E. Common Color-Forming Agents.....	844
II. Organic Reagents.....	845
A. General Aspects.....	845

1. Types of Reactions.....	845
a. Reactions Not Involving Valence Changes.....	845
b. Oxidation-Reduction Reactions.....	846
c. Reactions Involving Formation of a Complex Compound.....	847
2. Chelation.....	847
a. Introductory Theory.....	847
b. Ligand Groups.....	848
c. Chelate-Forming Metals.....	849
d. Stability of Inner Complexes.....	849
e. Steric Hindrance.....	849
f. Tautomerism.....	850
3. Analytical Applications.....	850
a. Acidity and Selectivity.....	850
b. Solubility.....	851
c. Precipitation.....	853
d. Masking.....	853
e. Titrimetry.....	854
f. Colorimetry.....	862
g. Extraction.....	863
B. Chelating Reagents.....	863
1. α -Dithiol Group.....	863
a. Toluene-3,4-dithiol (Dithiol).....	864
2. Diketones and Related Compounds.....	864
a. Acetylacetone.....	867
b. Thenoyltrifluoroacetone (TTA).....	868
3. 8-Quinolol and Its Derivatives.....	869
a. 8-Quinolol (8-Hydroxyquinoline, Oxine).....	869
b. Derivatives of 8-Quinolol.....	872
4. α -Acylloxime Group.....	873
a. α -Benzoinoxime (Cupron).....	874
5. α -Nitrosophenol Group.....	874
a. α -Nitrosophenol.....	875
b. 1-Nitroso-2-naphthol.....	875
c. Nitroso-R Salt.....	876
d. 2-Nitroso-1-naphthol.....	876
6. Thionalide (Thioglycolic Acid β -Aminonaphthalide).....	877
7. Dithiocarbamate and Xanthate Groups.....	878
a. Sodium Diethyldithiocarbamate.....	878
b. Diethylammonium Diethyldithiocarbamate.....	880
c. Potassium Ethyl Xanthate.....	881
8. Mercaptobenzothiazole.....	881
9. <i>p</i> -Dimethylaminobenzylidenerhodanine.....	882
10. Dithiooxamide (Rubeanic Acid).....	883
11. Dithizoné.....	884
12. Cupferron and Analogous Compounds.....	890
a. Cupferron.....	890
b. Neocupferron.....	893
c. Others.....	894
13. Dioxime Group.....	894
a. Dimethylglyoxime (Biacetylloxime).....	896
b. Cyclohexanedionedioxime (Nioxime).....	898
c. α -Furildioxime.....	898
14. Cuproine Group.....	898
a. 2,2'-Biquinoline (Cuproine).....	899
15. Ferriox Group.....	900
a. 1,10-Phenanthroline (<i>o</i> -Phenanthroline).....	900
16. Complexons.....	901
a. Ethylenediaminetetraacetic acid.....	902
(1) As a Masking Agent.....	904
(2) In Colorimetry.....	904
(3) In Titrimetry.....	904
(a) Direct Titrations.....	905
(b) Indirect Titrations.....	906

C. Salt-Forming and Miscellaneous Reagents.....	906
1. Arsonic Acids.....	906
2. Tannin.....	907
3. Thiourea Group.....	908
a. Thiourea (Thiocarbamide).....	908
References.....	909

SECTION C. Separation: Principles and Technics

22. Principles of Separations. By <i>Lockhart B. Rogers</i>	917
I. Introduction.....	919
A. Purpose and Scope of Chapter.....	919
B. Role of Separations in Analysis.....	919
C. Classifications of Separations.....	920
II. Basic Concepts.....	923
A. Goals of a Separation.....	923
B. Background for Calculations.....	923
C. Partition Terminology.....	925
III. Calculations.....	927
A. Outline of Types of Contacts.....	927
B. Crosscurrent Processes.....	928
1. Discrete Equilibrium Contacts.....	928
2. Differential Contact.....	931
C. Countercurrent Processes ("Fractionation").....	932
1. Fundamental Process.....	933
a. Discrete Equilibrium Contacts.....	933
(1) Binomial Distribution.....	933
(2) Gaussian Distribution.....	938
b. Continuous Contact—Poisson Distribution.....	940
c. Special Modification—Zone Refining.....	941
2. Single Withdrawal Process.....	942
a. Discrete Equilibrium Contacts.....	942
b. Continuous Contact.....	943
(1) HETP Approach.....	943
(2) Differential Approach.....	944
c. Special Modifications.....	944
IV. Special Topics.....	945
A. Optimal Conditions in Countercurrent Separations.....	945
1. Adjustments of Distribution Ratios.....	945
2. Reflux.....	946
B. Determinations of Partition Ratios.....	947
C. Distribution Behavior and Chemical Structure.....	947
D. Roles Played by Rates.....	948
E. Selection of a Separation Method.....	949
F. Continuous Separations.....	951
G. Principles Shared by Separations and Determinations.....	951
References.....	953
23. The Phase Rule in Analytical Chemistry. By <i>L. O. Case</i>	957
I. Introduction.....	959
A. Scope and Limitations of the Phase Rule.....	959
B. The Phase Rule as a Rule of Algebra.....	960
C. Outline of the Derivation of the Phase Rule.....	961
1. Phase.....	961
2. External Restraints.....	962
3. Phase Compositions. Components.....	963
4. Summation of the Phase Rule Variables.....	966
5. Equilibrium Relations.....	967
6. Final Result for the Phase Rule.....	968
7. Consequences of the Phase Rule Result.....	968

D. Phase Rule Diagrams.....	968
E. Revision of the Number of Phase Rule Variables.....	970
II. One-Component Systems.....	971
A. General Features.....	971
B. Tracing Phase Diagrams for One-Component Systems.....	973
1. Interpretation of the Diagram.....	973
2. The Critical Point.....	974
3. Other Variables.....	975
III. Two-Component Systems.....	975
A. General Features.....	975
B. Temperature-Composition Diagrams (at Constant Pressure).....	977
1. Two-Phase Equilibrium.....	977
2. Relative Amounts of Phases.....	979
3. Three-Phase Equilibrium.....	980
4. Relative Amounts of Phases. Phase Reactions.....	981
5. Other Invariant Terminations of Two-Phase Equilibrium.....	982
a. Loss of a Component.....	982
b. Azeotropic Invariance.....	983
c. Critical Invariance.....	984
C. Pressure-Temperature-Composition Diagrams.....	984
D. Analytical Applications.....	985
1. General Considerations.....	985
2. Construction of Temperature-Composition Diagrams.....	987
a. Thermal Analysis. Heating and Cooling Curves.....	987
(1) Theoretical Cooling Curves.....	988
(2) Actual Cooling Curves.....	990
b. Solubility Determination.....	991
3. Phase Separations.....	992
a. Pure Compounds or Pure Components.....	992
b. Phases of Variable Composition.....	995
(1) Fractional Distillation and Crystallization.....	995
4. Melting or Freezing Point as a Criterion of Purity.....	998
IV. Three-Component Systems.....	1000
A. Composition-Composition Diagrams. General Principles.....	1001
1. Two-Phase Equilibrium.....	1002
a. Relative Amounts of Phases. Tie Lines.....	1003
2. Three-Phase Equilibrium.....	1004
3. Other Types of Invariance.....	1006
4. The Equilateral Triangular Diagram.....	1007
5. Four-Phase Equilibrium.....	1009
6. Degenerate Cases.....	1011
B. Analytical Applications.....	1012
1. Introduction.....	1012
2. Construction of Composition-Composition Diagrams.....	1013
a. The Method of Wet Residues.....	1015
3. Separation of Phases.....	1016
4. Salting Out.....	1019
5. Multicomponent Systems.....	1019
6. Pressure-Temperature Diagrams.....	1020
a. Two-Component Systems.....	1021
b. Preparation of Pure Hydrates.....	1023
c. Other Applications.....	1024
V. Conclusion.....	1026
24. Decomposition and Dissolution of Samples: Inorganic. By Hobart H. Willard and Charles L. Rulfs.....	1027
I. Introduction.....	1027
II. Acids as Solvents.....	1033
A. Nonoxidizing Acids.....	1033
1. Action on Metals.....	1033

2. Solubility of Oxides.....	1035
3. Solubility of Carbonates.....	1036
4. Solubility of Sulfides.....	1036
5. Solubility of Sulfates.....	1037
6. Solubility of Phosphates.....	1037
7. Solubility of Silicates.....	1037
8. Action of Hydrochloric Acid at High Temperature and Pressure.....	1038
B. Oxidizing Acids.....	1039
III. Fusion Processes.....	1041
A. Nonoxidizing Alkaline Fluxes.....	1042
1. Fusion with Alkali Carbonates.....	1042
2. Fusion with Borax.....	1043
3. Fusion with Sodium or Potassium Hydroxide.....	1043
4. Sintering with Calcium Oxide.....	1044
B. Oxidizing Alkaline Fluxes.....	1044
C. Acid Fluxes.....	1045
1. Potassium Pyrosulfate.....	1045
2. Potassium Bifluoride.....	1046
3. Boric Oxide.....	1046
IV. Use of Chlorine or Bromine at High Temperatures.....	1047
V. Miscellaneous Processes.....	1048
References.....	1049
25. Decomposition and Dissolution of Samples: Organic. By <i>E. C. Dunlop</i> ...	1051
I. Introduction.....	1051
II. Decomposition of Organic Samples.....	1053
A. Dry Ashing Methods.....	1053
1. Crucible and Flame.....	1053
2. Crucible and Furnaces.....	1055
3. Tube Furnaces.....	1058
4. Oxygen Bomb.....	1061
5. Oxygen Flask.....	1062
6. Oxyhydrogen Burning.....	1063
7. Induction Heating.....	1064
B. Wet Ashing Methods.....	1065
1. Acids.....	1065
2. Mixed Acids.....	1065
3. Oxidizing and Reducing Agents.....	1068
a. Hydrogen Peroxide.....	1068
b. Persulfate.....	1069
c. Iodic and Chromic Acids (<i>Van Slyke Method</i>).....	1070
d. Chromic and Sulfuric Acids.....	1072
e. Carius Method (<i>Fuming Nitric Acid</i>).....	1073
f. Kjeldahl Method.....	1074
C. Special Reagents.....	1075
1. Peroxide Bomb.....	1075
2. Alkali Metal Fusion.....	1078
3. Alkali Metal in Solvents.....	1080
4. Lamp Method (<i>Combustible Solvents</i>).....	1081
5. Lime Fusion (<i>Liebig Method</i>).....	1083
6. Alkali Metal Complexes.....	1084
7. Miscellaneous Methods.....	1085
III. Dissolution of Organic Samples.....	1086
References.....	1090
26. Mechanical Methods. By <i>Harold C. Matraw</i> and <i>Fredric D. Leipziger</i>	1095
I. Introduction.....	1095
II. Methods Depending upon Exclusion Due to Size.....	1096
A. Filtration.....	1096
1. General.....	1096

2. Apparatus.....	1097
3. Filter Materials.....	1097
4. Technics.....	1099
B. Ultrafiltration.....	1099
C. Dialysis.....	1100
D. Molecular Sieves.....	1101
III. Methods Depending upon Differences in Size, Mass, or Density.....	1103
A. Sedimentation.....	1103
B. Centrifugation.....	1103
1. Ultracentrifugation.....	1103
C. Miscellaneous Technics.....	1104
1. Impaction and Impingement.....	1104
2. Flotation.....	1105
3. Decantation.....	1105
4. Micromanipulation.....	1106
5. Sieving and Screening.....	1106
IV. Methods Depending upon Other Physical Properties.....	1107
A. Magnetic Separation.....	1107
B. Sonics.....	1108
C. Thermal Separation.....	1108
D. Electrical Separation.....	1108
V. Effect of Particle Size on Separations.....	1109
References.....	1110
27. Diffusion Methods. By <i>A. Letcher Jones</i> and <i>Glenn R. Brown</i>	1113
I. Introduction.....	1113
II. Separation by Thermal Diffusion.....	1116
A. Fundamentals of Techniques.....	1116
B. Theories Describing Molecular Migration.....	1118
C. Operation of Thermal Diffusion Equipment.....	1120
1. Batch Thermal Diffusion Equipment.....	1120
2. Single Batch Columns.....	1120
3. Multiple-Column Batch Systems.....	1124
4. Continuous Thermal Diffusion Equipment.....	1126
5. Flow Patterns in Continuous Thermal Diffusion Equipment.....	1127
6. Mechanical Forms of Continuous Equipment.....	1128
D. Separative Efficiency of Thermal Diffusion Columns with Various Flow Patterns.....	1130
E. Applications of Thermal Diffusion to Separation.....	1135
1. Separation of Simple Hydrocarbon Mixtures.....	1135
2. Separation of Complex Hydrocarbon Systems.....	1143
F. Summary of Thermal Diffusion.....	1150
III. Separations by Barrier Diffusion Processes.....	1150
A. Fundamentals of Technique.....	1150
B. Gaseous or Vapor Separations through Barriers.....	1152
C. Barrier Permeabilities.....	1153
D. Gas-Vapor Separations.....	1154
E. Vapor-Vapor Separations.....	1156
F. Liquid Separations.....	1156
References.....	1157
28. Electromigration and Electrophoresis. By <i>John R. Cann</i>	1159
I. Introduction.....	1159
II. Theory of Electromigration.....	1160
III. Moving Boundary Electrophoresis.....	1167
A. Principle of Moving Boundary Electrophoresis.....	1168
B. The Tiselius Electrophoresis Apparatus.....	1170
C. Analysis and Interpretation of Electrophoretic Patterns.....	1175
D. Electrophoresis as a Criterion of Purity.....	1183
E. Electrophoresis of Interacting Systems.....	1187

F. Analysis of Low Molecular Weight Substances	1192
G. Preparative Moving Boundary Electrophoresis	1193
H. Other Applications	1194
IV. Electrophoresis-Convection	1194
A. Principles	1195
B. Fractionation Procedures	1196
C. Applications of Electrophoresis-Convection	1198
D. Electrogravitational Separations	1200
V. Zone Electrophoresis and Ionophoresis on Supporting Media	1201
A. Principles of Zone Electrophoresis	1202
B. Apparatus and Procedures	1206
C. Applications of Zone Electrophoresis	1211
D. Electrochromatography	1214
E. Immuno-electrophoresis	1216
VI. Electrophoretic and Isoelectric Separations in a Density Gradient	1216
VII. Other Preparative Methods	1219
A. Compartment Apparatus	1219
B. Electrodialysis	1221
C. Recent Developments in Continuous Electrophoresis	1224
VIII. Microscopic Electrophoresis	1225
References	1227
29. Distillation. By <i>Arthur Rose</i>	1235
I. Introduction	1236
II. Nomenclature and Apparatus	1243
III. Operating Variables	1248
A. Relative Volatility	1249
1. Theory of Vaporization	1252
B. Reflux Ratio	1253
C. Theoretical Plates	1254
IV. Simple Distillation without a Column	1259
A. Volatilization, Vaporization, and Sublimation	1262
V. Fractional Distillation with a Column	1264
A. Effect of Operating Variables	1265
1. Effect of Relative Volatility; Number of Theoretical Plates, and Reflux Ratio	1265
2. Effect of Charge Composition	1266
3. Effect of Holdup	1267
4. Effect of Pressure	1269
B. Start-Up Practice	1269
C. Choice of Procedure	1271
VI. Molecular Distillation	1271
VII. Accuracy and Precision in Analytical Distillation	1275
VIII. Analytical Applications	1277
A. Typical Analytical Distillation	1277
B. Some Common Applications	1279
1. Organic Materials	1280
2. Inorganic Materials	1281
3. General and Miscellaneous Applications	1282
References	1282
30. Vacuum Methods. By <i>William S. Horton</i>	1285
I. Introduction	1285
II. Means of Measurement—Vacuum Gages	1286
III. Means of Production—Pumps	1290
IV. Auxiliary Equipment and Techniques	1292
V. Related Physical Properties	1297
VI. Some Specific Techniques	1301
References	1307

