CHEMICAL SERIES

Experimental , Physical Chemistry

by Farrington Daniels
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INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, Ph.D., Consulting Editor

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EXPERIMENTAL PHYSICAL CHEMISTRY

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The late Dr. H. P. Talbot was consulting editor of the series from its inception in 1911 until his death in 1927. Dr. James F. Norris was consulting editor from 1928 until his death in 1940. Dr. Louis P. Hammett became joint consulting editor in January, 1940.

PREFACE TO THE THIRD EDITION

This revision introduces many new experiments and revises others in an attempt to keep abreast of the rapid developments in physical chemistry. Some of the former experiments have been eliminated or expanded because they have found their way into earlier courses and are already known to students, who each year come better prepared for the study of physical chemistry.

A certain amount of elasticity is needed in the amount of laboratory work covered in a single experiment, depending on the time and equipment that are available and on the experience and capacity of the student. When an experiment is too short, the student will find interesting things to do under "Suggestions for Further Work"; when it is too long, the instructor will select parts of the "Procedure" which may be omitted. Several of the procedures have been expanded and the directions made more specific without sacrificing the development of self-reliance on the part of the student, which has always been one of the aims of this book.

The discussion of more advanced apparatus and techniques in Parts II and III is relatively less complete than before because so much excellent new material is being published and because more specialized reference books for the laboratory, particularly in organic chemistry and physics, are now available.

The authors are glad to acknowledge the many helpful suggestions that have come from Professor W. E. Roseveare, Dr. T. F. Anderson, Mr. Milton Goff, Mr. A. E. Edwards, Mr. Lee K. Henke, and many students and others.

They are indebted to Mr. Henry H. Schmalz, a student in the course, for the helpful new drawings.

Farrington Daniels, J. Howard Mathews, John Warren Williams.

Madison, Wis., July, 1941.

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PREFACE TO THE FIRST EDITION

To illustrate the principles of physical chemistry, to train in careful experimentation, to develop familiarity with apparatus, to encourage ability in research—these are the purposes of this book.

The imperative is not used. Procedures are described but orders are not given. The student must study the experiment first and then set his own pace—a method which develops both his power and his interest.

Some of the experiments are new, some are based on researches described in the literature, and some are classical. Considerable choice is available and selection will be made on the basis of available apparatus and on the maturity and ultimate aims of the student.

The second part of the book describes apparatus and technique, particularly for more advanced work. It is designed not only to encourage students to undertake special work but to aid them in later years in the solution of practical problems. No claim whatsoever is made for completeness. In their selection of material the authors have been guided simply by their own experience.

In a large class, several different experiments must go on at the same time and many of them are necessarily performed before the material has been studied in class. For this reason, space is devoted at the beginning of each experiment to a brief statement of the theory involved.

The experiments are based on the experience of several years at the University of Wisconsin where thirty to thirty-five experiments are assigned during the year and an average of eight hours of laboratory time is allowed for each. Many of the experiments can be done in less time, and the student is urged to follow the suggestions given for further work. Particular encouragement is given for original work.

Farrington Daniels, J. Howard Mathews, John Warren Williams.

Madison, Wis., October, 1929.

EXPERIMENTAL PHYSICAL CHEMISTRY

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COMMENTS CONCERNING LABORATORY WORK

In general, every determination should be made in duplicate. One cannot rely too heavily on a single experiment, because it may contain an accidental mistake. Close checks do not necessarily guarantee accuracy, since the same error may be repeated, but if duplicate results do not check the experiment is obviously unsatisfactory. Check experiments are more valuable if they are carried out under widely different conditions.

Any experiment worth doing is worth a careful report. Accurate reports should become a habit. They should include a discussion of the theory, the derivation of all formulas, and the original data. They should be neat, systematic, and unbiased. A true scientist cannot let his data be influenced by a preconceived hypothesis, nor must a student be influenced in his calculations by a knowledge of the correct result.

If the data are suitable for graphing, they are plotted neatly on coordinate paper and a curve is drawn, using a ruling pen and India ink.

The accuracy of the results should be critically evaluated, and, whenever possible, the averaged value of the measurements compared with the accepted value in the tables mentioned below. centage error is then calculated whenever justifiable.

The International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1928-1933) contain the best constants, critically evaluated by experts. Landolt-Börnstein's "Physikalisch-Chemische Tabellen" contain a great number of experimental constants but they have not been critically evaluated. The "Tables Annuelles" published in English by the McGraw-Hill Book Company, Inc., are valuable also. For useful tables, Van Nostrand's "Chemical Annual," the "Handbook of Physics and Chemistry" published by the Chemical Rubber Company, and Lange's "Handbook of Chemistry" published by Handbook Publishers, Inc. Sandusky, Ohio, are recommended.

For advanced technique in physical chemistry the worker is referred to Parts II and III of this book or to the original literature or to the following treatises: Reilly, Rae, and Wheeler, "Physico-chemical Methods" (D. Van Nostrand Company, Inc., New York, 1940); Strong, "Procedures in Experimental Physics" (Prentice-Hall, Inc., New York, 1939); Morton, "Laboratory Technique in Organic Chemistry" (McGraw-Hill Book Company, Inc., New York, 1938).

EXPERIMENT NUMBERS

To facilitate the use of the new book with laboratory schedules based on the second edition, the corresponding experiment numbers of the two editions are listed here. Old experiments which have been changed considerably are given in italics. Minor changes have been made in many of the experiments.

Second edition	Third edition	Second edition	Third edition	Second edition	Third edition	Second edition	Third edition
1	1	18	20	39	42	59	
2	2	19	21	40	43	60	. 58
3		20	22	41	44		59
4	3	21	23	42	45		60
	4	22	24	43	46		61
5	5	23	25	44		61	
6	6	24	26	45	47	62	
7		25	27	46		63	
	7		28	47	54	64	62
8	8	26	29	48	50	65	63
9	9	27	30	57		66	
10	10	28	35	49	48	67	64
11	11	29	36	50			65
12	12	30	37	51	49	68	66
	13	31	33	52	51	69	69
	14	32	31	53		70	67
13	15	33	32	54	52		68
14	16	34	34	55	53	71	70
15	17	35	38	56	57		71
	18	36	39		55	. (,	72
16		37	40		56	100	
17	19	38	41	58			

The following more or less classical experiments are recommended to cover important principles or techniques when only a limited time is available for laboratory work: 2, 5, 10, 15 or 16, 22, 25, 31 or 32, 38 or 39, 44, 49, 53, 67 or 69.

The following experiments may be done without any special equipment beyond ordinary glassware, balance, thermometer, etc.: 2, 3, 5, 6A, 7, 8, 16, 19, 20, 21, 23, 25, 26, 27, 29, 30, 32, 33, 34, 35, 37, 38, 40, 41, 42, 43.

The following experiments may be of special interest to students of the biological sciences: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 22, 25, 26, 29, 39, 43, 49, 50, 51, 61, 65, 66, 67, 71.

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PART I LABORATORY EXPERIMENTS

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