

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

EXPERIMENTAL PHYSICAL
CHEMISTRY

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

EXPERIMENTAL PHYSICAL CHEMISTRY

BY

W. G. PALMER, M.A., Sc.D., D.Sc.

*Fellow of St John's College, Cambridge
formerly University Lecturer in Chemistry
in the University of Cambridge*

SECOND EDITION

CAMBRIDGE
AT THE UNIVERSITY PRESS

1962

Cambridge University Press
978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition
W. G. Palmer
Frontmatter
[More information](#)

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, Delhi

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521104951

© Cambridge University Press 1962

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without the written
permission of Cambridge University Press.

First edition 1941
Reprinted with corrections 1946, 1949, 1954
Second edition 1962
This digitally printed version 2009

A catalogue record for this publication is available from the British Library

ISBN 978-0-521-05903-9 hardback
ISBN 978-0-521-10495-1 paperback

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

Contents

	<i>page</i>
Preface	vii
Symbols and conventions	x
References to literature	xii
Introduction	1
Calibration	3
<i>Chap.</i> I. The densities of gases and vapours	10
II. Crystallization and the properties of crystals	30
III. Solutions and solubility	52
Simple solutions	53
Mutual solubility	77
IV. Dilute solutions	113
Determination of molecular weight in solution	113
Experiments illustrating semi-permeability and osmosis	132
The distribution of solutes between solvents	138
V. Thermochemistry	154
VI. Ionization	176
The conductance of electrolytic solutions .	179
Electromotive force	193
Hydrogen-ion indicators and buffer solu- tions	229

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

vi

CONTENTS

	<i>page</i>
<i>Chap.</i> VII. Velocity of chemical reaction	243
VIII. Surface chemistry	268
Appendices	
1. Notes on apparatus	309
2. Data on the preparation, composition, etc. of common reagents	310
Index	311
Tables of logarithms	318

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

Preface

In planning the course of work contained in this book I have tried to keep the following considerations before me. First, that students both at Universities and in schools cannot often afford to devote more than limited periods to practical work in any one scientific subject. The provision of detailed instructions is therefore imperative, in order that a satisfying result may be reached without a discouraging waste of time. Secondly, that while being capable of yielding reasonable accuracy, the apparatus ought to be simple enough to be assembled or constructed by the students themselves from ordinary laboratory equipment. Further, that an approach to many important principles through the laboratory, rather than by way of the lecture, more easily stimulates interest, and more certainly ensures comprehension.

Most of the exercises have for many years past formed part of a course of physical chemistry at the University Chemical Laboratory at Cambridge. While much of the course has been found suitable for beginners in the subject, who are candidates for an Honours Degree through the Natural Sciences Tripos, a number of experiments are described which are appropriate to more advanced students. The limitations of time (which for beginners usually consists of periods not longer than three hours) have influenced the choice and nature of the experiments, necessitating, even if it were not desirable upon other grounds, the simplicity of home-made apparatus, and sometimes the substitution of rough-and-ready means of observation for less direct methods, which would overtax both the time and the experience of the beginner. I hope that a course of this type may interest teachers and students in other

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

viii

PREFACE

Universities and Colleges, and that the simplicity of the equipment required in many of the experiments may render them suitable for Higher Certificate and Scholarship forms in schools.

While the notes introducing each chapter are not intended to replace the use of adequate text-books on the theory of the subject, it may be hoped that if the student can readily refer to principles while at work on a problem, he will more easily interweave practical wisdom with theoretical knowledge, and come to realize that the former is the real foundation of the latter. The inclusion of completely worked examples of nearly all the experiments has been made a regular feature. These examples are all based upon data obtained in the Cambridge laboratory from actual materials and apparatus described in the text. They will justify their inclusion if they elucidate difficulties in the most direct way, demonstrate the possible accuracy attainable, and assist in encouraging an orderly and significant exposition of the data. I should be grateful to receive helpful suggestions from teachers and students who may use the book, but I venture to counter the criticism that the practical instructions are so detailed as to impugn the students' initiative, by remarking that if a beginner spends the greater part of his limited laboratory period in merely prospecting an experiment, with no satisfying result, discouragement will commonly overshadow all that he may well have learnt in manipulation.

In a laboratory where all one's fellow-teachers are also one's friends and well-wishers, it is very difficult to offer thanks to some rather than to all, but I must specially mention the help I have received in discussion on Chapter VIII (Surface Chemistry) from Professor Lennard-Jones, and from Mr G. E. Briggs (of the Cambridge Botany School); from Dr R. C. Evans on Chapter II (The Properties of Crystals), and

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

PREFACE

ix

from Mr A. J. Berry and Dr T. P. Hoar on Chapters v, vi, and vii (Thermochemistry, Ionization and Reaction Velocity). All of these friends have been good enough to read parts of the book in MS. or proof. I am indebted to my son, R. G. Palmer, for the estimations upon which fig. 12 is based. I also feel bound to pay homage to the memory of Dr H. J. H. Fenton, whose teaching, with its masterly blend of enthusiasm, scholarship, and scepticism, it was a rare privilege to receive. To the staff of the Cambridge University Press I also owe a large debt of gratitude, both for their patient solicitude, and their unrivalled expertness, which has so greatly improved the tenor of the book.

W. G. P.

June 1941

Largely through the agency of those who, having found *Experimental Physical Chemistry* acceptable in their teaching, have afforded me the assistance of their friendly and constructive criticisms, I have been enabled to introduce some minor emendations and improvements into this new impression, notably on pp. 32, 238 and 245.

W. G. P.

May 1951

Preface to Second Edition

The principal task in preparing a new edition has been the reviewing of data and references in the light of recent progress in chemistry. In consequence many of the data have needed some adjustment, and new references have superseded a majority of those formerly appearing. Where changes have been made in the text it is hoped that improvement has resulted.

W. G. P.

Nov. 1961

SYMBOLS AND CONVENTIONS

List of symbols

- A area, molecular surface area, gas-density correction.
 a activity (especially of electrolytes).
 α degree of (electrolytic) dissociation.
 β conductance ratio.
 C, c molecular concentration; number of components (phase rule); equivalent concentration.
 c specific heat, molecular heat.
 D, d density (all states of matter).
 E e.m.f.; electrode potential; energy (general).
 η coefficient of viscosity.
 F force; number of degrees of freedom (phase rule).
 F faraday.
 f activity coefficient.
 G free energy ($H - TS$); temperature coefficient of reaction velocity.
 g osmotic coefficient (electrolytes).
 H heat content (ΔH , heat change at constant pressure).
 K, K_c, K_p equilibrium constant (concn. or press. terms).
 κ specific conductance.
 L, l latent heat; latent heat per g.
 l ionic mobility (ionic conductance); liquid phase (phase rule).
 Λ equivalent conductance.
 M molecular weight.
 μ ionic strength.
 N, n number of (g.) molecules
 N_A molar fraction (of A).
 P, p pressure; number of phases (phase rule); partial pressure.
 ϕ coefficient of fluidity.
 R gas constant per mol. per degree.
 R, ρ resistance; specific resistance.
 S entropy; percentage of solute in solution.

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

SYMBOLS AND CONVENTIONS

xi

- s solid phase (phase rule).
 σ molecular cross-section; surface tension (surface free energy).
 T, t absolute temperature; temperature Centigrade; time.
 τ time interval.
 U total energy (ΔU , heat change at constant volume).
 V, v volume, dilution; partial volume.
 $V, mV.$ volt; millivolt.
 W work.
 w weight.
 z ionic charge.
 Z collision frequency.

Mathematical and chemical signs

- | | |
|----------------------------------|---------------------------------|
| \simeq approximately equal to. | $[A]$ concentration of (A). |
| $\Delta(A)$ change of (A). | xN x normal solution. |
| $\log x = \log_{10} x.$ | b.p. boiling-point. |
| $\log_{10} e = 0.4343.$ | f.p. freezing-point. |
| $\ln x = \log_e x.$ | m.p. melting-point. |
| $\log_e 10 = 2.303.$ | |

*Fundamental constants (chemical scale)**

- Avogadro number, N , 6.023×10^{23} .
 Faraday, F , 96,494 coulombs (abs.).
 Electronic charge, e , 4.803×10^{-10} e.s.u.
 Gas constant, R , 0.08205 litre-atmosphere per mol. per degree; 1.986 calories per mol. per degree; 8.314 joules per mol. per degree.
 Molecular volume of a perfect gas at N.T.P. 22.415 litres.
 Absolute zero of temperature -273.16° .

* Cohen *et al.*, *Rev. Mod. Phys.*, **27**, 363 (1955).

Cambridge University Press

978-0-521-10495-1 - Experimental Physical Chemistry, Second Edition

W. G. Palmer

Frontmatter

[More information](#)

REFERENCES TO LITERATURE

- Acta. chem. Scand.* Acta chemica Scandinavica.
Amer. Min. American Mineralogist.
Ann. Physik. Annalen der Physik (Leipzig).
Arch. phys. biol. Archives de physique biologique.
Arch. Sci. phys. nat. Archives des Sciences physiques et naturelles (Geneva).
Atti. R. Accad. Lincei. Atti (Rendiconti) della reale Accademia dei Lincei.
Ber. Berichte der deutschen chemischen Gesellschaft.
Biochem. Z. Biochemische Zeitschrift.
Bull. Soc. chim. France. Bulletin de la Société chimique de France.
Can. J. Chem. Canadian Journal of Chemistry.
Chem. Soc. Abstr. Abstracts of the Chemical Society or British Chemical Abstracts.
Gazzetta. Gazzetta chimica italiana.
I.C.T. International Critical Tables.
Ind. Eng. Chem. Industrial and Engineering Chemistry.
Inst. Metals. Ann. Diag. Institute of Metals, Annotated Diagrams.
J. Amer. Chem. Soc. Journal of the American Chemical Society.
J. Chem. Physics. Journal of Chemical Physics.
J. Chem. Soc. Journal of the Chemical Society (London).
J. chim. physique. Journal de chimie physique (Geneva).
J. Gen. Physiol. The Journal of General Physiology (Baltimore).
J. Physical Chem. The Journal of Physical Chemistry.
J. prakt. Chem. Journal für praktische Chemie.
J. Soc. Chem. Ind. Journal of the Society of Chemical Industry.
Kolloid-Z. Kolloid-Zeitschrift.
Monograph Amer. Chem. Soc. Monographs of the American Chemical Society (Reinhold Publishing Corp. U.S.A.).
Natl. Bur. Stand. National Bureau of Standards (U.S.A.).
Natl. Bur. Stand. J. Res. National Bureau of Standards (U.S.A.), Journal of Research.
Phil. Mag. Philosophical Magazine (London, Edinburgh and Dublin).
Phil. Trans. Philosophical Transactions of the Royal Society.
Proc. phys. Soc. Proceedings of the Physical Society.
Proc. Roy. Soc. Proceedings of the Royal Society (London).
Quart. Rev. Quarterly Reviews (Chemical Society).
Rec. Trav. chim. Recueil des Travaux chimiques des Pays-Bas.
Rev. Mod. Phys. Reviews of Modern Physics.
Trans. Electrochem. Soc. Transactions of the Electrochemical Society.
Trans. Faraday Soc. Transactions of the Faraday Society.
Z. anal. Chem. Zeitschrift für analytische Chemie.
Z. angew. Chem. Zeitschrift für angewandte Chemie.
Z. anorg. Chem. Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem. Zeitschrift für Elektrochemie.
Z. Krist. Zeitschrift für Kristallographie.
Z. physikal. Chem. Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.