

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

PHYSICAL CHEMISTRY
EXPERIMENTAL AND THEORETICAL

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

PHYSICAL CHEMISTRY

EXPERIMENTAL AND THEORETICAL

An Introductory Text-book

BY

G. VAN PRAAGH

B.Sc. (Lond.), Ph.D. (Cantab.), A.Inst.P.

*Head of the Science Department of
Christ's Hospital, Horsham*



CAMBRIDGE
AT THE UNIVERSITY PRESS
1950

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

CAMBRIDGE
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781107586277

© Cambridge University Press 1950

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 published 1950

First paperback edition 2015

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

ISBN 978-1-107-58627-7 Paperback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

PREFACE

It is hoped that this book will meet the need for a laboratory manual of experiments in physical chemistry suitable for school and college use. The limited time and equipment usually available render impracticable many physical chemistry experiments described in existing text-books. A number of these have here been simplified and adapted: they have all been thoroughly tried out and, in many cases, specimen results are quoted that have been obtained by students using the experimental methods and apparatus described in the text.

Many students do not begin to get a real understanding of a new subject until they observe the phenomena for themselves in the laboratory. In this book, therefore, each topic is introduced by means of a few short experiments designed to demonstrate in a simple manner the subject-matter of the section. These experiments are followed by brief theoretical sections. An outline of the historical development of the subject is included where possible, because this often throws considerable light on the present state of knowledge and theory. At the end of each section, a number of other experiments are described, some of which at least the student should perform for himself. More experiments are included than would normally be done by any one student in an introductory course.

The choice of topics to be included in the subject of physical chemistry is somewhat arbitrary: in fact several of them are treated both in physics and in chemistry text-books. The selection made here is governed by the suitability of the various topics for experimental treatment in school or college laboratory. Hence a few that are often included in text-books of physical chemistry have here been omitted. For example, the experimental work on radioactivity, optical spectra, X-ray spectro-

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

vi

PREFACE

scopy and the mass spectrograph leading to our knowledge of atomic structures, is omitted as being too complex to be reproduced in an introductory course. On the other hand, the classical atomic theory, on which the science of theoretical chemistry is largely based, is treated more fully than usual. In the author's opinion, the history of the atomic theory in the first half of the nineteenth century is rarely given the place of importance it merits, and, in view of the complex and rather confused manner in which the theory developed, it is not surprising that students often do not have a clear understanding of its significance.

The treatment is throughout from the point of view of the kinetic-molecular theory rather than that of the laws of thermodynamics. The mathematics have been kept simple: emphasis is rather laid on the physico-chemical phenomena themselves and their significance in various branches of science such as metallurgy, chemical syntheses, analytical methods, biology, mineralogy and so on. There are already many written exercises and calculations published in other text-books and therefore none have been included here.

I wish to express my thanks to Dr J. A. Kitchener for reading the proofs and making many valuable suggestions, and to my pupil, J. F. Duke, who drew most of the diagrams. I should also like to thank the Publishers for helpful criticisms of the manuscript and for the trouble they have taken in preparing it for the press. The loan of blocks for the following figures is gratefully acknowledged: Messrs Macmillan, Figs. 38, 40, 77, 104, Messrs Longmans, Figs. 84 and Plate 4*a* and *b*.

G. VAN PRAAGH

CHRIST'S HOSPITAL,
HORSHAM
June 1950

Cambridge University Press
 978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
 An Introductory Text-book
 G. Van Praagh
 Frontmatter
[More information](#)

CONTENTS

<i>List of Plates</i>		<i>page ix</i>
<i>List of Experiments</i>		xi
Chapter 1	THE GASEOUS STATE	1
Chapter 2	THE LIQUID STATE	15
	(a) Condensation of gases, p. 15. (b) Vapour pressure, p. 20. (c) Boiling, p. 25. (d) Liquid surfaces, p. 29.	
Chapter 3	THE SOLID STATE	36
	(a) Equilibrium between the liquid and solid states, p. 36. (b) The crystalline state, p. 38. (c) Polymorphism, p. 47. (d) Phase diagrams, p. 51.	
Chapter 4	ATOMS AND MOLECULES	61
	(a) The atomic theory, p. 61. (b) The relative weights of the atoms, p. 69. (c) Valency forces, p. 81.	
Chapter 5	SOLUTIONS	87
	(a) The vapour pressure of solutions, p. 87. (b) The boiling-point of solutions, p. 91. (c) The freezing-point of solutions, p. 94. (d) Osmosis, p. 99.	
Chapter 6	ELECTRICAL PROPERTIES OF SOLUTIONS	108
	(a) Electrical conductance of liquids, p. 108. (b) Specific and equivalent conductance, p. 117. (c) Migration of ions, p. 124. (d) Conductometric titrations, p. 131.	
Chapter 7	ADSORPTION	134
Chapter 8	THE COLLOIDAL STATE	144
	(a) Colloidal solutions, p. 144. (b) The stability of sols, p. 148. (c) Gels, p. 156. (d) Emulsions, p. 161.	
Chapter 9	CHEMICAL CHANGE	164
	(a) Thermochemistry, p. 164. (b) The effect of concentration on reaction rate, p. 168. (c) Temperature coefficient of reaction rates, p. 176. (d) Catalysis, p. 180. (e) Reversible reactions, p. 187.	

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

viii

CONTENTS

**Chapter 10 MASS ACTION AND THE IONIC
DISSOCIATION THEORY** *page* **198**

(a) The strengths of acids, p. 198. (b) The common ion effect, p. 203. (c) Indicators, p. 207.

Chapter 11 PHASE RELATIONS **216**

(a) A gas and a liquid, p. 216. (b) Two liquids, p. 218. (c) Mixtures of a salt and water, p. 233. (d) Mixtures of two solids, p. 243. (e) The distribution law, p. 257.

Chapter 12 ELECTROCHEMISTRY **263**

(a) The electrochemical series of the metals, p. 263. (b) Voltaic cells, p. 270. (c) Single electrode potentials and concentration cells, p. 275. (d) Galvanic couples, p. 287.

Bibliography **291**

Index **293**

Cambridge University Press
 978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
 An Introductory Text-book
 G. Van Praagh
 Frontmatter
[More information](#)

LIST OF PLATES

- Plate 1* **PHOTOMICROGRAPHS OF
CRYSTALS** *facing page 42*
- (a) Cubes of common salt. ($\times 10$.)
 - (b) Common salt crystallized in the presence of a trace of urea, showing cubic and octahedral faces. ($\times 15$.)
 - (c) Rhombic sulphur, crystallized from carbon disulphide. ($\times 10$.)
 - (d) Copper sulphate (triclinic). ($\times 10$.)
 - (e) Beryl (hexagonal). Synthetic emeralds. ($\times 5$.)
 - (f) Quartz (trigonal), showing prism and pyramid faces. ($\times 10$.)
 - (g) Calcite (trigonal). Two crystals are arranged on a hair to show the two images formed by double refraction; a third crystal is placed with its optic axis in the direction of the hair and in this case only one image is formed. ($\times 10$.)
- Plate 2* **DENDRITES AND CRYSTAL
GRAINS** **44**
- (a) Dendrites of lead nitrate crystallized from water showing cubic terminations. ($\times 50$.)
 - (b) Dendritic growth of ammonium chloride crystals from solution in water. ($\times 25$.)
- Plate 3* **LIESEGANG PHENOMENA** **161**
- (a) Magnesium hydroxide bands in gelatine. ($\times \frac{1}{2}$.)
 - (b) Silver chromate bands. ($\times \frac{3}{2}$.)
 - (c) Banded agate. ($\times 1$.)
- Plate 4* **SOLID SOLUTIONS** **246**
- (a) 50% Copper-nickel alloy, etched to show dendritic structure. ($\times 86$.)
 - (b) Silver-copper alloy showing dendrites of copper-silver solid solution lying in a silver-copper eutectic. ($\times 200$.)
 - (c) Zoned plagioclase feldspar (solid solutions of sodium and calcium aluminosilicates). (Crossed nicols, $\times 50$.)

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book
G. Van Praagh
Frontmatter
[More information](#)

LIST OF EXPERIMENTS

Chapter 1

- 1–4. Diffusion of gases.
5. Molecular motion in mercury vapour.
6. Boyle's law.
7. Charles's law.
8. The air thermometer.
9. Dalton's law of partial pressures.
10. Measurement of rates of diffusion.

Chapter 2

- (a) 1, 2. Liquefaction of gases by cooling.
3. Diffusion in liquids.
- 4, 5. Liquefaction of gases by pressure.
6. Brownian motion.
- (b) 1, 2. Existence of vapour pressure.
3. Measurement of vapour pressure at different temperatures.
4. Latent heat of vaporization.
- (c) 1. Boiling-point.
2. Determination of boiling-points. Siwoboloff's method.
3. Determination of boiling-points. Emich's method.
4. Change of boiling-point with pressure.
- (d) 1. Surface tension.
- 2, 3. The spheroidal state.
4. Measurement of surface energy.
- 5, 6. Surface films on water.
7. Monolayers on water.

Chapter 3

- (a) 1. Determination of freezing-point.
2. Determination of melting-point.
- (b) 1. The crystalline state.
2. The crystal systems.
3. The effect of foreign substances on crystal form.
4. Crystallization.
5. Super-cooling.
6. Effect of rate of crystallization on purity.
- 7–12. Experiments on isomorphism.
- (c) 1. The polymorphism of mercuric iodide.
2. Transition-point determination. Colorimetric method.
3. Transition-point determination. Dilatometric method.
4. Liquid crystals.

Cambridge University Press
978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
An Introductory Text-book

G. Van Praagh
Frontmatter

[More information](#)

xii

LIST OF EXPERIMENTS

Chapter 4

- (a) 1. Atomic theory. Introductory experiment.
2–4. The law of multiple proportions.
- (b) 1. The volume composition of hydrogen chloride.
2. The volume composition of ammonia.
3. Vapour density determination. Victor Meyer's method.
- (c) 1. The compound of ammonia and aluminium chloride.
2. The action of hydrogen chloride on water.

Chapter 5

- (a) 1–3. The vapour pressure of solutions.
4. Molecular weight by lowering of vapour pressure.
- (b) 1. The boiling-point of solutions.
2. Molecular weight by elevation of boiling-point.
- (c) 1. The freezing-point of solutions.
2–4. Molecular weight by depression of freezing-point.
5. Molecular weight by depression of freezing-point, Rast's method.
- (d) 1–5. Demonstrations of osmosis.
6. Air as a semi-permeable membrane.

Chapter 6

- (a) 1, 2. Electrical conductance of liquids.
3. Faraday's laws of electrolysis.
4. The law of multiple proportions for electricity.
- (b) 1, 2. Specific and equivalent conductance.
3. Conductance measurements with Kohlrausch bridge.
- (c) 1, 2. The migration of ions.
3. Transport number determination.
4. Measurement of ionic mobility.
- (d) 1–4. Conductometric titrations.

Chapter 7

- 1, 2. Adsorption of gases by solids.
3, 4. Adsorption from solution.
5, 6. Adsorption on freshly formed precipitates.
7. The Freundlich adsorption isotherm.
8. Adsorption reagents.
9. Adsorption indicators.
10. Exchange adsorption.
11. Preferential adsorption: chromatography.
12. Preferential adsorption at liquid-liquid interfaces.

Chapter 8

- (a) 1–3. The properties of colloidal solutions.
4–8. The preparation of colloidal sulphur, arsenious sulphide, ferric hydroxide, silver and gold.

LIST OF EXPERIMENTS

xiii

- (b) 1–3. The precipitation of sols.
4. Protective colloids.
5. The precipitation of sols by electrolytes.
6. The preparation of colloidal platinum by Bredig's method.
7. Measurement of cataphoretic velocity.
8. Electric endosmosis.
9. Smoke precipitation.
- (c) 1–3. Some typical gels.
4–6. The preparation of gels of silica, calcite and common salt.
7. Soap gels in alcohol.
8. Soap gels in oil.
9. The peptization of soap gels.
10, 11. Liesegang phenomena.
- (d) 1. Emulsions.
2. Emulsifying agents.
3. Emulsion types.

Chapter 9

- (a) 1, 2. Relative stability.
3. Heats of reaction.
4. Heats of neutralization.
- (b) 1. The effect of concentration on rate of reaction.
2. The rate of decomposition of sodium thiosulphate solutions.
3. The rate of saponification of an ester.
4. The kinetics of the reaction $2\text{HI} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{I}_2$.
- (c) 1. The effect of temperature on rate of reaction
2. The temperature coefficient of the rate of decomposition of sodium thiosulphate solutions.
3. The temperature coefficient of the reaction 9b–4.
- (d) 1–4. Some examples of catalysis.
5. The catalytic effect of copper ion on the oxidation of hydriodic acid by dichromate.
6. An autocatalytic reaction.
7. The reaction between potassium permanganate and oxalic acid.
- (e) 1, 2. Reversible reactions.
3. The effect of pressure on the equilibrium position of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.
4. The reversible reaction $\text{FeCl}_3 + 3\text{NH}_4\text{CNS} \rightleftharpoons \text{Fe}(\text{CNS})_3 + 3\text{NH}_4\text{Cl}$.
5. The heterogeneous equilibrium between silver chloride and ammonia.

Chapter 10

- (a) 1, 2. The relative strengths of acids.
3. Measurement of the ionization constant of a weak acid.
- (b) 1–3. The common ion effect.
4. Solubility product.
5. Measurement of the solubility product of silver acetate.
- (c) 1–4. Experiments with indicators.
5. Measurement of pH by indicators.
6. The pH of salt solutions.

Cambridge University Press
 978-1-107-58627-7 - Physical Chemistry: Experimental and Theoretical:
 An Introductory Text-book

G. Van Praagh
 Frontmatter

[More information](#)

xiv

LIST OF EXPERIMENTS

- (c) 7. Experiments with a universal indicator:
- i. Dilution of a strong acid.
 - ii. pH of salt solutions.
 - iii. The common ion effect.
 - iv. The hydrolysis of an ester.
 - v. Changes in pH during electrolysis.
 - vi. Buffer solutions.

Chapter 11

- (a) 1. The solubility of a gas in a liquid.
 2. Determination of the solubility of ammonia in water.
- (b) 1. The miscibility of liquids with water.
 2. The critical solution temperature for phenol and water.
 3. The boiling-point of 'mixtures' of two immiscible liquids.
 4. Determination of the molecular weight of chlorobenzene by steam distillation.
 5. The boiling-points of mixtures of alcohol and water.
 6. The fractionation of a mixture of benzene and xylene.
 7. Investigation of a maximum boiling-point mixture.
 8. The preparation of standard hydrochloric acid from the maximum boiling-point mixture.
 9. The preparation of absolute alcohol.
- (c) 1. The system water:potassium nitrate.
 2. The solubility curve of potassium nitrate.
 3. The freezing-points of solutions of potassium nitrate.
 4. The system water:calcium chloride.
 5. Determination of the transition-point of sodium sulphate thermometrically.
 6. The vapour pressures of the hydrates of copper sulphate.
- (d) 1. Mixed melting-points.
 2. The construction of temperature:composition diagrams by the melting-point method.
 3. The construction of temperature:composition diagrams by the cooling-curve method.
 4. The phase diagram for mixtures of tin and lead.
- (e) 1, 2. The distribution of iodine between benzene and water.
 3. Investigation of the equilibrium $KI + I_2 \rightleftharpoons KI_3$.

Chapter 12

- (a) 1, 2. The electrochemical series of the metals.
- (b) 1. The voltaic pile.
 2. A simple voltaic cell.
 3. The Daniell cell.
- (c) 1. Measurement of relative electrode potentials.
 2. The e.m.f. of copper concentration cells.
 3. The e.m.f. of hydrogen concentration cells.
 4. Measurement of the pH of solutions.
 5, 6. Electrometric titrations.
- (d) 1. The decomposition of water by a galvanic couple.
 2. The rusting of iron.