

**TEXT-BOOK OF  
PHYSICAL  
CHEMISTRY**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649270538

Text-book of physical chemistry by Clarence L. Speyers

Except for use in any review, the reproduction or utilisation of this work in whole or in part in any form by any electronic, mechanical or other means, now known or hereafter invented, including xerography, photocopying and recording, or in any information storage or retrieval system, is forbidden without the permission of the publisher, Trieste Publishing Pty Ltd, PO Box 1576 Collingwood, Victoria 3066 Australia.

All rights reserved.

Edited by Trieste Publishing Pty Ltd.  
Cover @ 2017

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form or binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

[www.triestepublishing.com](http://www.triestepublishing.com)

**CLARENCE L. SPEYERS**

**TEXT-BOOK OF  
PHYSICAL  
CHEMISTRY**



Chem  
S7527te

TEXT-BOOK  
OF  
PHYSICAL CHEMISTRY

BY  
CLARENCE L. SPEYERS  
ASSOCIATE PROFESSOR OF CHEMISTRY, RUTGERS COLLEGE



NEW YORK  
D. VAN NOSTRAND COMPANY  
23 MURRAY AND 27 WARREN STREETS  
1897

363394  
23. 2. 39.

Copyright, 1907,  
By D. VAN NOSTRAND COMPANY.

---

ELECTROTYPED BY J. S. CUSHING & Co., NORWOOD, MASS.

## PREFACE.

---

EXCEPTING the chapter on Phases, this book represents what I have been in the habit of teaching the Senior Class in the Chemical Course at Rutgers College. I find lectures very unsatisfactory. The subject needs much thought, and the student does not seem able to get the proper material for this from notes, unless the lectures are made mere dictations. Besides, Physical Chemistry has attained such development that it is well to put a certain part of it in permanent text-book form now, for whatsoever changes in our views time may bring, certain ideas we now have will not change. These fundamental ideas I have tried to put into this little book. Of course, I have also included some theories and ideas that later on may have to be rejected. That cannot be helped.

It is difficult to separate that which should be considered in a book of this kind from that which should be excluded. I have tried to give the most important principles, rather than mere facts, sometimes in the text, sometimes in the problems. As yet there are hardly any theories connecting light energy and so-called chemical energy; so light relations have been entirely omitted. For like reasons, crystallography has been omitted. It did not seem best to leave out matters which have been brought under strict discipline for the sake of

taking in those which have not yet been so organized. There is not room for both here.

I have not attempted to give a historical development of any subject, but have presented the subject in what I thought the clearest way, sometimes adopting one person's view in one part of a subject, another's view in another part, and perhaps my own in still another part. So I find it impossible in my lectures and in this book to state who was the first to develop any particular theory, or to discover any particular fact. I refer the student to Ostwald's *Lehrbuch d. Allgemeinen Chemie*; Nernst's *Theoretische Chemie*; Gibbs's *Equilibrium of Heterogeneous Substances*; *Zeitschrift f. Phys. Chemie*. All of these have been freely used in preparing this text-book.

I have adopted the view that matter is a collection of energies in space, considering the relations of the energies to be the prime object of investigation. With Ostwald, I feel confident that the materialistic interpretation has passed its prime and has no promise for the future. Still, as this is a text-book, I give the prominent materialistic views of the present time.

This book is intended for self-instruction of course, as well as for class-room use. Whoever works through it conscientiously, paying particular attention to the problems, will get a very fair idea of Physical Chemistry.

C. L. S.

September, 1897.



# CONTENTS.

## CHAPTER I.

	PAGE
SOME GENERAL REMARKS ON ENERGY . . . . .	1
1. Physical chemistry. 2. Chemical change. 3. Force. 4. Energy. 5. Matter. 6. Energies. 7. Kinetic energy. 8. Space energy. 9. Surface energy. 10. Volume energy. 11. Heat energy. 12. Electric energy and magnetic energy. 13. Radiant energy. 14. Factors of energies. 15. Conditions of equilibrium. 16. Persistence of the factors. 17. Measurement of energy. 18. Available energy.	

## CHAPTER II.

GASES . . . . .	16
19. Volume energy. 20. Perfect gas. 21. Factors of volume energy. 22. Mechanical theory of gases. 23. Van der Waals' theory. 24. Critical quantities.	

## CHAPTER III.

HEAT . . . . .	24
25. Units of heat. 26. Thermodynamics. 27. Internal energy. 28. Specific heat. 29. First law of thermodynamics. 30. Heating of solid and liquid. 31. Heating of vapor and gas. 32. Internal energy of a gas. 33. Mechanical equivalent of heat. 34. Difference between molecular heats under constant pressure and at constant volume. 35. Available energy from the expansion of a gas; no heat supplied from without. 36. Second law of thermodynamics. 37. Change of internal energy with the temperature.	

## CHAPTER IV.

	PAGE
PHYSICAL CHANGES . . . . .	40

38. Physical changes. 39. Fusion. 40. Sublimation. 41. Vaporization. 42. Solutions. 43. Gaseous solutions. 44. Solid solutions. 45. Liquid solutions. 46. Henry's law. 47. Liquids in liquids. 48. Vapor pressure of solutions. 49. Fractional distillation. 50. Surface energy. 51. Determination of molecular weights of liquids. 52. Available volumes of liquids. 53. The state of a substance in solution. 54. Osmotic pressure and temperature. 55. Avogadro's law. 56. Various expressions for the osmotic pressure. 57. Molecular weights of dissolved bodies. 58. Liquid and vapor. 59. Molecular weights of bodies which give off vapor when in solution. 60. Heat of solution. 61. Heat of dilution and available energy.

## CHAPTER V.

EQUILIBRIUM . . . . .	87
-----------------------	----

62. Equilibrium. 63. Conditions of equilibrium. 64. Equilibrium in gaseous systems. 65. Equilibrium in liquid systems. 66. Equilibrium in solid systems. 67. Equilibrium in solid-gas systems. 68. Equilibrium in liquid-gas systems. 69. Equilibrium in solid-liquid systems. 70. Partition of a substance between two solvents. 71. Determination of molecular weights by depression in solubility of one liquid in another.

## CHAPTER VI.

CHEMICAL KINETICS . . . . .	125
-----------------------------	-----

72. Chemical kinetics. 73. Monad reactions. 74. Diad reactions. 75. Triad reactions. 76. Number of molecules in a reaction.

## CHAPTER VII.

PHASES . . . . .	132
------------------	-----

77. Conditions of equilibrium. 78. Coexistent phases. 79. Monad systems. 80. Diad systems. 81. Thermodynamic relations.

CONTENTS.

vii

CHAPTER VIII.

	PAGE
WHEN TEMPERATURE IS VARIABLE . . . . .	148
82. The general equation for variable temperature. 83. Decomposition producing vapors. 84. Solution. 85. Decomposition of a gas. 86. Change in velocity with the temperature.	

CHAPTER IX.

ELECTROCHEMISTRY . . . . .	154
87. Units. 88. Ohm's law, Faraday's law, Joule's law. 89. Ions. 90. Conductivity or absorption of electricity by solutions. 91. Cause of the ionic state. 92. Measuring the electric conductivity or absorption of electricity by solutions. 93. Migration of the ions. 94. Absolute velocity of the ions. 95. Conductivity or absorption in terms of velocity. 96. Conductivity or absorption and concentration. 97. Temperature and conductivity or absorption. 98. Absorption by melted salts and solids. 99. Force acting on the ions. 100. Cause of potential difference. 101. Chemical and electric energy. 102. Experimental measurement of $V$ . 103. Source of the electric energy. 104. Potential difference and ionic tension. 105. Cells with active solutions. 106. Gas cells. 107. Ionisation of water. 108. The chemometer. 109. Potential difference between simple cells of different concentration. 110. Potential difference between solutions. 111. Polarization. 112. Constant cells. 113. Electrolytic separations. 114. Electrochemical analysis. 115. Accumulators.	

CHAPTER X.

Ions . . . . .	208
116. Some general properties of the ions. 117. Heat of ionisation. 118. Formation of ions.	