A SYSTEM OF PHYSICAL CHEMISTRY. VOLUME III

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A system of physical chemistry. Volume III by William C. McC. Lewis & James Rice

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WILLIAM C. MCC. LEWIS & JAMES RICE

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TEXTBOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.

AND

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BY

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BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL

IN THREE VOLUMES

VOLUME III

QUANTUM THEORY

(WITH TWO APPENDICES BY JAMES RICE, M.A., LECTURER IN PHYSICS IN THE UNIVERSITY OF LIVERPOOL)

NEW IMPRESSION

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PREFATORY NOTE.

In this volume an attempt is made to deal with some physico-chemical applications of the principles of statistical mechanics. An account is first given of the application of what is now known as the classical statistical mechanics, more particularly to the problem of the energy content of substances and its variation with temperature, on the one hand, and to the problem of radiation on the other. It will be seen that in both these branches classical statistical mechanics makes it possible for us to advance very considerably beyond the limits set by the elementary kinetic theory employed in Volume I., but at the same time it will be found that the classical statistical mechanics does not furnish us with a complete and adequate basis for all the observed phenomena. It is therefore necessary to enlarge or modify the fundamental concepts of statistical mechanics, and it is precisely with this object in view that Planck has been led to introduce the idea of quanta. Planck's quantum theory is, therefore, properly speaking, a new or modified system of statistical mechanics. It happens, however, that Planck was led to his revolutionary changes by considerations based upon the observed facts of radiation, and for this reason it is usual to speak of the quantum theory of radiation. Radiation affords, as a matter of fact, one illustration, and a very striking one, of the applicability of the new mechanics. But even the success which has attended Planck's treatment of radiation problems would scarcely have sufficed to gain for his views that prominence which they now have, had it not been for the satisfactory explanation which his theory offers at the same time for the heat content of substances and the variation of the heat content with temperature. The idea of energy quanta has been applied in recent years to other types of physico-chemical phenomena, some of which will be considered. It will be assumed, in the treatment of the subject-matter dealt with in this volume, that

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the reader is familiar with the principles of elementary kinetic theory and the principles of thermodynamics already discussed in Volumes I. and II. Such of these principles and results as may be required will be introduced therefore without further explanation.

It will be observed that there is a change of attitude in the mode of dealing with the experimental material in this volume as compared with the attitude adopted in the preceding volumes. The theoretical concepts made use of in Volumes I. and II. have become classical to a large extent, and the treatment resolves itself into a brief account of underlying principles followed by a systematic application of these principles to phenomena characteristic of systems which had attained equilibrium or were tending towards equilibrium. In the present volume, however, the underlying ideas—especially those involved in the quantum theory—have not as yet been fully accepted, at least in their present form. The position of the quantum theory is to a certain extent undefined. The physical significance of what is meant by a quantum of energy or, in a stricter sense, the quantum of action, is still vague. The present position has been summarised by Professor Bragg in the words: "His [Planck's] hypothesis is not so much an attempt to explain as a focussing of all the difficulties into one; so that, if this master difficulty is overcome, a number of others melt away". In view of what has just been said, it will be readily appreciated that many of the experimental investigations referred to in the present volume have been carried out primarily with the object of testing the validity of the quantum hypothesis itself, and as this can be done most effectively by the intensive examination of certain relatively restricted fields of research, the information available at the present time is of a somewhat detached character as compared with the variety and generality of the phenomena to the interpretation of which the simple kinetic theory and the principles of thermodynamics have been applied. For this reason, therefore, relatively little stress is laid upon the system of classification already adopted in Volumes I. and II. Naturally with the progress of investigation it will become feasible ultimately—provided the quantum hypothesis becomes generally accepted—to classify phenomena as has been done in the preceding volumes; but for the present the interest centres elsewhere, *viz.* on the validity of the underlying hypothesis itself. It is well that the reader should appreciate this state of affairs at the outset.

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