TREATISE ON INORGANIC CHEMISTRY

I

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VOLUME I

INTRODUCTION AND MAIN GROUPS OF THE PERIODIC TABLE

ABBREVIATED CONTENTS OF VOLUME II

PREFACE

Since its first German edition in 1931, this book has been repeatedly revised and supplemented in accordance with the progress of chemistry; but its original plan has proved entirely satisfactory as a framework for new knowledge. In particular the systematic treatment of inorganic substances on the basis of the Periodic System has so far proved its worth as to have found its way into many other textbooks. Equally successful, when dealing with particular classes in each group, has been found the method of giving first a general introduction and then, before the detailed discussion of each substance, a survey of such topics of wider significance as may present themselves in its connection.

It is likely that future textbooks will give increasing prominence to the behaviour of groups of substances, as opposed to the discussion of individual ones; and in successive editions of this book, such chapters have become more numerous and fully developed. Each starts from some special property which for its further explanation needs the general theory, or else points the way to it. Thus is taken into account the line of thought of the chemist, progressing from particulars to generalities; and such knowledge then throws further light on subsequent problems.

The present translation is based essentially on the 7th and 8th German editions, but with further revision, improvement and supplementation before translation; notably in the sections on the chemical bonds, radioactivity, nuclear chemistry and the transuranic elements. I am very grateful to Professor J. S. Anderson, F.R.S., for the translation, carried out with great keenness and insight into the author's mind, and for suggesting many valuable improvements and additions to meet the needs of the wider circle of readers to whom the book is now addressed. And to the Editor, Professor Kleinberg, for his great interest my thanks are equally due.

Hamburg, October 1955 H. REMY

TRANSLATOR'S FOREWORD

During the past ten or fifteen years there has been a marked resurgence of interest in inorganic chemistry in Great Britain and the United States. The need for a detailed understanding of the chemical relationships between the elements in many pure and applied research problems has become apparent, and increased attention has been given to the chemistry of the elements in university courses. In consequence, many have felt the need for a comprehensive text in the English language setting out the subject in its present state of development. Such a work needs to cover the whole of the factual material and to bring it into proper relationship with the relevant thermodynamic, kinetic and structural data.

Amongst German texts, successive editions of Remy's *Lehrbuch der anorganischen Chemie* have gone far to meet this need, and it is to be hoped that this translation will prove valuable to a wide circle of readers. The translation has been based upon Professor Remy's latest revision of this standard work, and has been brought up to date as far as is practicable in a rapidly changing field of activity. With the author's permission, a few passages have been modified by the translator. Thermodynamic conventions have been changed where necessary, to follow American usage.

The author is indebted to Mr. J. D. M. McConnell B.Sc. for undertaking the task of proof correction, and for his care in the final preparation of the text.

Melbourne, September 1955 J. S. ANDERSON

SOME IMPORTANT PHYSICAL CONSTANTS

Absolute temperature of the melting point of ice, $T_{0°C} = 273.16°K$.

Atmosphere (normal pressure), 1 atm. = $1.013250 \cdot 10^{6}$ dyne cm^{-2}.

Avogadro's number, $N_A = 6.0238 \cdot 10^{23}$.

Boltzmann's constant, $k = 1.38026 \cdot 10^{16}$.

Elementary quantum of electricity, $e = 4.8022 \cdot 10^{-10}$ e.s.u. $= 1.60186 \cdot 10^{-20}$ e.m.u. $= 1.60186 \cdot 10^{-19}$ coulomb.

Specific charge on the electron $= \frac{e}{m} = 1.7591 \cdot 10^{8}$ coulomb g^{-1}.

Units of energy

1 erg = 10^{-7} joules (watt-seconds) $= 2.777778 \cdot 10^{-14}$ kWh $= 0.239006 \cdot 10^{-7}$ cal.

1 liter-atmosphere $= 1.013278 \cdot 10^{9}$ erg $= 101.3278$ joules $= 2.81466 \cdot 10^{-5}$ kWh $= 24.2180$ cal.

1 cm^3atm. $= \frac{1 \text{ l-atm.}}{1000.028} = 0.101325$ joules $= 2.81458 \cdot 10^{-8}$ kWh $= 2.42177 \cdot 10^{-2}$ cal.

1 cal (thermochemical gram-calorie) = 4.1840 joule = 1.16222 kWh = 0.041292 l-atm. = 41.293 cm^3atm.

1 $cal_{15°}$ (15° calorie) = 4.1855 joules = 1.00036 cal.

1 ev (electron-volt) $= 1.6020 \cdot 10^{-19}$ joules $= 3.829 \cdot 10^{-20}$ cal.

1 ev per molecule is equivalent to 23.064 kcal per mol.

Energy of a light quantum (photon) of wave length λ cm, $\frac{hc}{\lambda} = \frac{1}{\lambda} \cdot 1.98574 \cdot 10^{-16}$ erg $= \frac{1}{\lambda} \cdot 1.23954 \cdot 10^{-4}$ ev.

This corresponds to $\frac{1}{\lambda} \cdot 11.9617$ joules per mol or $\frac{1}{\lambda} \cdot 2.85892$ cal per mol.

Faraday (electrical charge per gram equivalent), 1 $\mathfrak{F}$ = 96493 coulombs. This represents 26.804 ampere-hours.

Gas constant, $R = 0.082054$ l-atm. = 8.3144 joules = 1.9872 cal.

Velocity of light, $c = 2.9979 \cdot 10^{10}$ cm sec^{-1}.

Liter (volume of 1 kg of air free water at its temperature of maximum density), 1 l = 1000.028 cm^3.

Molar volume of ideal gas (at 0°, 760 mm pressure) = 22.414 l = 22414.5 cm^3.

Acceleration of gravity (normal value, at sea level and 45° latitude), $g_0 = 980.665$ cm sec^{-2}.

Quantum of action (Planck's constant), $h = 6.6238 \cdot 10^{-27}$ erg sec.

Smythe factor $\left(= \frac{\text{physical atomic weight}}{\text{chemical atomic weight}}\right) = 1.000279$.

INTRODUCTION

Chemistry is concerned with the occurrence, isolation and artificial preparation of the different sorts of matter; with the study of their composition, properties, and reactions; and with the systematics and the reasons for the phenomena observed.

From analysis of the various sorts of matter presented to us in nature, it has been concluded that the whole known material world is formed from a limited number of fundamental sorts of matter—the *chemical elements*. A chemical element was formerly defined as a substance which could not be resolved by chemical means. However, it has been found that it is not always possible to delimit the concept of an element with sufficient precision by this criterion of resolvability. A chemical element is now defined as a species of matter of which all the atoms bear *the same nuclear charge* (cf. p. 1). When it became possible, by processes directly affecting the nucleus of the atom, to alter the charge on the nucleus, and thereby to transform atoms of one element into atoms of another element (cf. Vol. II, Chap. 13), it became possible to prepare elements which do not occur in Nature. Including these artificially produced elements (the products of nuclear transformations), 101 different species of atoms, differing in their nuclear charge, are now known with certainty—i.e., 101 chemical elements are now known (cf. Table II, Appendix). Only 91 of these have been detected in Nature.

One of the chemical elements plays a special role in the living world—namely, *carbon*. All living organisms consist of carbon compounds, some of great complexity. The part of chemistry which is particularly concerned with the compounds of carbon is therefore called *organic chemistry*. As distinct from this field, the study of the composition, properties, reactions, etc., of the whole material world, in so far as it does not properly fall within the subject of organic chemistry, is called *inorganic chemistry*.

Even among the compounds of carbon, it is usual to class as *organic compounds* only those which, in composition, structure and properties are related to the carbon compounds of importance for living organisms. This includes, admittedly, the great majority of the compounds of carbon, but there is a considerable number of carbon compounds which are quite different from these in composition and structure, and therefore in properties—for example, the metallic carbides. Such carbon compounds are regarded as *inorganic compounds*. 'Carbon compounds' and 'organic compounds' are thus not identical concepts. Elementary carbon also falls within the scope of inorganic chemistry, while its simplest compounds (especially its oxides and the acids derived therefrom, and the simplest hydrocarbons) are closely related both to organic and inorganic compounds. It is therefore usual to discuss these compounds in both inorganic and organic chemistry.

The aim and content of *inorganic chemistry* are concerned with the extraction and utilization of the different elements, and with a knowledge of their chemical individuality (i.e., with the occurrence, preparation and properties of the elements and their compounds). It treats also of the general and systematic laws deduced from a comparison of the elements with one another, and of the causes which, in the ultimate analysis, underlie the observed properties and behavior.

There are other branches of chemistry which overlap both organic and inorganic chemistry. The particular field of *analytical chemistry* is the study and application of those properties and reactions of matter which make it possible to decompose a substance into its constituents. It is then possible to determine whether a substance is simple or compound in nature, and to determine the proportions of its constituents. *Synthetic chemistry* is sometimes set in contrast with this, as the science which builds up substances from their constituents. It is now more usual to take *preparative chemistry* as the antithesis of analytical chemistry. Preparative chemistry, of which synthetic chemistry is a part, comprises the preparation of substances, with the techniques involved. It includes not only the preparation of compounds from simple substances, but also the preparation of elements from compounds—a by no means unimportant aspect of preparative inorganic chemistry. The methods and apparatus which are used in industry for chemical operations, form part of *chemical technology*, which deals also with the applications and methods of testing the substances manufactured. *Industrial chemistry* merges into chemical technology, in so far as it treats of the organization and operation of the chemical industry; it is also concerned with the economic importance of raw materials and the products derived from them by chemical processes.

There are also other important special branches of chemistry. *Electrochemistry* deals with the use of the electric current in carrying out chemical reactions. *Photochemistry* deals with the effects of light on chemical change. *Colloid chemistry* is the study of the properties of matter in a state characterized by a certain range of particle size (cf. Vol. II). *Radiochemistry* deals with the chemistry of radioactive substances, and such of their properties as are significant for chemistry. *Nuclear chemistry* is the study of the transformations of atomic nuclei, and of the properties and behavior of artificially produced species of atoms. *Crystal chemistry* is the study of the relation between crystal structure and chemical constitution. *Geochemistry* is concerned with the composition of the earth, and the principles underlying the terrestrial distribution of the elements. *Metallography* employs special experimental methods which have found application in other parts of chemistry. Mention should also be made of the *history of chemistry* as an important and instructive branch of the science.

In so far as they are concerned with inorganic substances, these branches of chemistry form part of the wider subject of inorganic chemistry. They will be dealt with in such scope as seems appropriate in a book covering the whole field of inorganic chemistry.

Mathematics and physics are the sciences which are most valuable subsidiary subjects in the study of chemistry. Some knowledge of the fundamental ideas of *crystallography* is also indispensable, and for an understanding of certain parts of chemistry an acquaintance with mineralogy and geology, or with the biological sciences, is also profitable.

During the last century, the application of physical methods and of mathematical reasoning created a new branch of science, *physical chemistry*. The principal objects of this subject lie in the quantitative application of physical methods to substances and reactions, with a view to discovering general laws, and deducing the behavior of matter from simple fundamental principles (e.g., from the laws of thermodynamics). It is not possible to draw a sharp line of distinction between the proper scope of physical chemistry, as compared with physics or with general chemistry, the more so as, during the last few decades, physical methods have been applied increasingly in all parts of chemistry. This is especially true of inorganic chemistry, so that it is no longer possible to present the subject from a modern and scientific standpoint without making extensive use of the results of physico-chemical investigations.

The field of study of inorganic chemistry is very wide. It comprises more than 100 elements, no two of which are exactly identical in behavior, and the enormous number of compounds which these elements form with one another. A survey of this wide field, and a grasp of those facts which are significant, can be made easier by organizing the multiplicity of facts in a suitable way. Such a synoptic viewpoint is provided by the Periodic System. This is based on the observed periodicity of chemical properties among the elements and—as will shortly be shown—it can be regarded as an inherently natural classification of the elements. Before considering the individual elements and their most important compounds, we shall therefore discuss the Periodic System. A consideration of the regularities which it reveals furnishes, at the same time, a brief survey of some of the most important properties of the elements and their compounds.

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Chapter 12. Fourth Main Group of the Periodic System: Carbon-Silicon Group