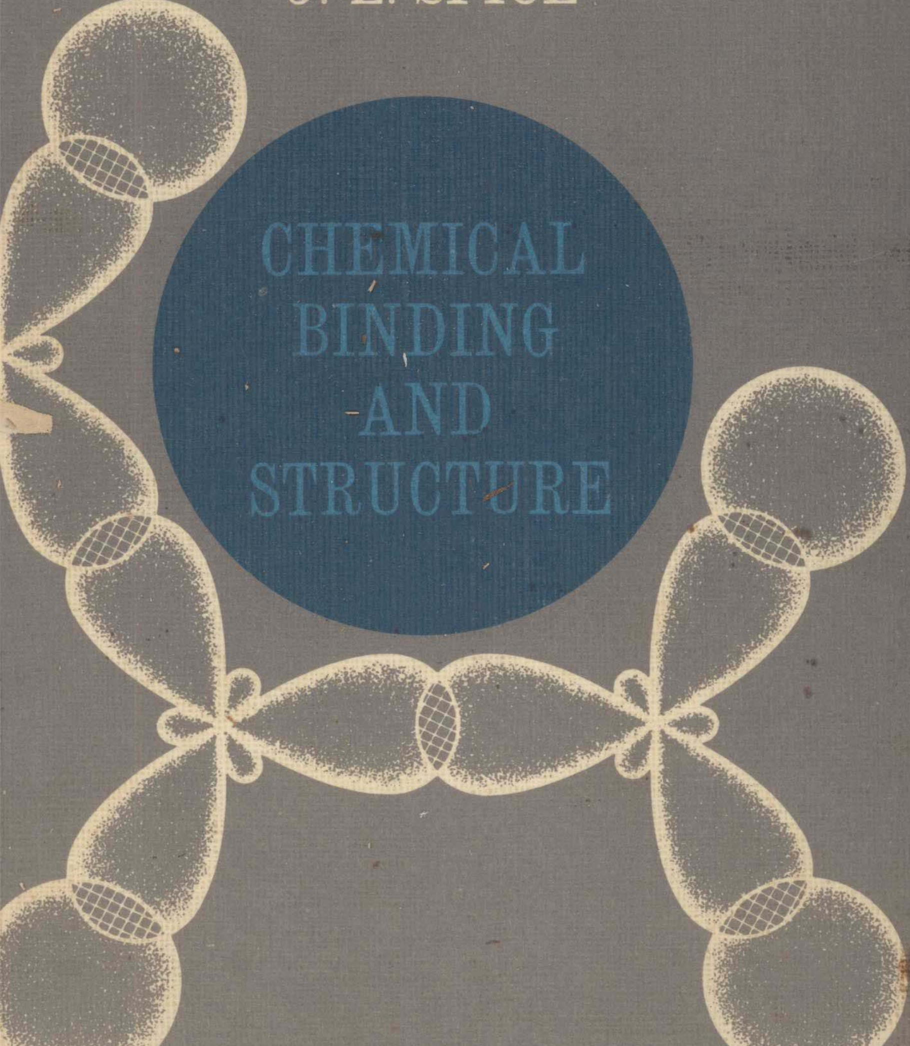
J. E. SPICE



CHEMICAL BINDING AND STRUCTURE

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GENERAL INTRODUCTION

The volumes in this division have been planned to provide a comprehensive treatment of chemistry at the intermediate level—that is, the sixth-form/first-year university level. Readers are assumed to have a background of O-level chemistry and of O- or A-level physics, and a working knowledge of elementary mathematics.

The books of the division will meet all the requirements of the recently revised A-level syllabuses of the examining boards, and an attempt has been made to anticipate the nature of future revisions of these syllabuses. They will also cover the ground for university scholarships, and for first-year university examinations, such as those set to intermediate, medical, engineering students, etc. They will provide ordinary national certificate students in technical colleges with all they need, and will constitute a useful background and companion to the studies of higher national candidates. In the U.S.A., first- and second-year college students will find them directly relevant to their studies and they will be of value to high-school students for reference purposes.

The present book assumes a knowledge of general atomic theory, as provided in the volume *Atomic Theory and the Structure of the Atoms.* It will serve not only as an account of Chemical Binding and Structure in its own right, but also as a companion to the volumes: *Chemistry of the Non-Metallic Elements* and *Chemistry of the Metallic Elements.*

PREFACE

This book is an account of chemical binding and structure in terms of current chemical theory. It has been planned and written so that sixth-formers can understand it, but it should also be useful to undergraduates and technical college students, as a concise qualitative account of an important subject. It will be found suitable for introductory chemistry courses in American colleges and universities. It is reasonably comprehensive in the range of phenomena covered, but it makes no attempt at comprehensiveness in the examples quoted. Full use is made of the ideas of wave mechanics, but there is no more than a mention of the formal methods of this technique. Binding and structure cannot be considered apart from energy changes; accordingly, there are discussions of energetics wherever relevant.

Some chemists, both in schools and in universities, think that school chemistry should not much concern itself with recent developments and theories; they deplore the arrival of freshmen at the university who know little descriptive chemistry, but are replete with half-digested "modern theories". It is certainly true that school chemistry must lay an adequate factual foundation for future work, but it is quite unrealistic to expect either the keen student or the enthusiastic teacher to eschew discussion of the ideas and discoveries which have made modern chemistry such an exciting science. And it is sometimes forgotten that wave mechanics is now thirty-seven years old! On the other hand, it is all too easy for an author to write a hurried description of modern valency theory, and then think he can explain the whole of chemistry in terms of it. Wave mechanics is not an easy subject, and if its essential ideas are to be thoroughly understood in a qualitative manner—as they certainly can be—very careful explanation and discussion is necessary. Moreover, it is altogether too facile to deal with problems of chemical stability and reactivity merely in terms of bonding; both kinetic and equilibrium factors play an essential part. In this book an attempt has been made to avoid the misinterpretations and oversimplifications found in some texts at this level. Although the treatment is largely qualitative, some of the examples at the end will be found to point the way to a more quantitative development.

The general plan of the book is sufficiently indicated by the table of contents. The last three chapters, which deal with methods of determining crystal and molecular structures, stand apart from the first ten. They have been included because it seemed desirable to tie a largely theoretical discussion as closely as possible to experimental techniques.

The author's debt to various well-known text-books is perhaps too obvious for there to be any need to particularise. He is grateful to Dr. A. G. Sharpe for making detailed comments on the manuscript, and pointing out sundry errors of fact and obscurities of interpretation. Most of the relevant passages have been amended, but the author remains unrepentant over his definition of a transition element.

Winchester, 1964 JOHN SPICE

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J. E. S.

CONTENTS

1 THE OLD AND NEW QUANTUM THEORIES

PROTONS, NEUTRONS, ELECTRONS AND ATOMS

Chemistry deals with matter, and with the ways in which one kind of matter can be changed into other kinds. It is known that all matter is built up from one or more of about one hundred different kinds of atom, and that the diverse properties of such things as chalk and cheese, rubber and nylon, glass and mild steel, etc., are ultimately determined by the atoms of which these substances are composed, and the patterns in which they are arranged. Before these patterns can be appreciated, the nature of the forces which bind atoms together must be understood. These forces, in turn, cannot be understood without some knowledge of the structure of the atom.

All atoms are composed of three fundamental particles, the proton, the neutron, and the electron. The proton and the neutron each have roughly the same mass as that of the hydrogen atom, while the electron has about 1/1840 of this mass. The neutron is electrically neutral, while the proton and electron carry equal positive and negative charges. The fact that 1 g of hydrogen contains about 6×10^{23} hydrogen atoms, and that protons, neutrons and electrons are very much smaller than hydrogen atoms, gives some idea of the minute size of these particles. Atoms consist of a very small, massive, and positively charged nucleus composed of protons and neutrons, together with enough electrons to balance the nuclear charge. Nuclear radii are of the order of 10^{-13} cm, while atomic radii are of the order of 10^{-8} cm. In fact, a special unit—the Angstrom unit—is used when dealing with atomic and molecular magnitudes; one Angstrom unit, written 1 Å, is 10^{-8} cm.

Atomic Numbers, Mass Numbers, and Isotopes

From the chemical point of view, the most important characteristic of an atom is its atomic number Z, which is the number of protons in the nucleus (that is, the nuclear charge) and hence also the number of electrons. The atomic number determines most of the chemical and physical properties of atoms in bulk, and is different for different elements. Atomic numbers were originally deduced by Rutherford from his scattering experiments with α-particles and metallic foils, and since then have been determined from X-ray spectra. Of naturally-occurring elements, uranium has the greatest atomic number, $Z = 92$, so that there can be just 91 elements coming before uranium. All but four of these elements occur naturally, and the missing four have now been made by nuclear reactions, as have eleven elements with atomic numbers greater than uranium. Details of all this work are discussed in two other volumes of this series: *Atomic Theory and the Structure of the Atom* and *Nuclear and Radio Chemistry*, both by T. A. H. Peacocke.

The mass of an atom is, practically speaking, the mass of its nucleus, and its mass number A, is the total number of protons and neutrons in the nucleus. For a given number of protons—that is, for a given atomic number—the number of neutrons can vary within certain limits, so that there can be atoms of the same element with different masses, called isotopes. When an element is a mixture of isotopes, its chemically-determined atomic weight is the weighted mean of the isotopic weights. Nuclear masses and structures are naturally of cardinal importance in connection with radioactivity and other nuclear changes, but for questions of chemical bonding and structure they are much less important. In this book, it will usually be possible to consider each atom simply as a nucleus of charge $+Z$, around which are Z electrons.

THE OLD QUANTUM THEORY AND ITS APPLICATION TO ATOMS

The Photoelectric Effect and the Quantum Theory

It is impossible to understand chemical forces without the quantum theory, which may almost be described as the atomic theory of energy. One of the phenomena which led to the quantum theory was the photoelectric effect (as used today in photoelectric cells) discovered by Hertz in 1887. He observed that negatively-charged particles, soon identified as electrons, were emitted when light of certain frequencies impinged on the surface of metals. For each metal there was a threshold frequency. Light of lower frequency, however intense, caused no emission of electrons, while as the frequency was increased beyond the threshold value, the energy of the electrons also increased. The effect can be studied with the apparatus of Fig. 1. The potential between the plates C and A is increased until the flow of electrons, as shown by the galvanometer G, just stops. From the measured

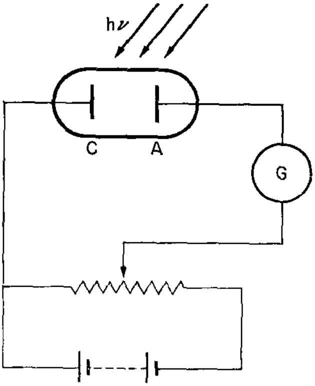

FIG. 1. *The photoelectric effect.*

value of this potential, the energy of the electrons can be calculated. When the light intensity is increased, the number of electrons emitted (as shown by the galvanometer reading), but not their energy, is also increased.

In 1887 light was thought to be a form of wave motion, with its energy proportional to its intensity, in turn proportional to the square of its amplitude, but independent of its frequency. Plainly, the photoelectric effect cannot be explained on this theory. Einstein, in 1905, suggested that in some respects light was more like a stream of particles, which he called "photons". Each photon corresponded to a small packet of energy, whose magnitude was equal to $h\nu$. h was a universal constant known as Planck's quantum of action, with the value $6{\cdot}63 \times 10^{-27}$ erg-sec, while ν was the frequency of the light. Unless each energy quantum was at least equal to the energy needed to expel an electron from the metal, no photoelectric emission could occur. Nor could smaller quanta be allowed to accumulate until the total energy was large enough. If, however, the energy quanta were greater than the threshold energy, the excess energy would be carried off by the electrons. Increasing the intensity of the light increased the number of quanta, and hence the number of electrons emitted, but not their energy. By experiments with the apparatus of Fig. 1, it is possible to find both h and the threshold energy for the metal of plate C.†

The most important result of the experiments just described, was that the old corpuscular theory of radiation, proposed by Newton but apparently disproved in favour of the wave theory by such phenomena as interference and diffraction, came to be resurrected—though in a very different form. Light (whether visible or ultraviolet) appeared to be *propagated* as wave-motion, but its *absorption* by metals seemed better to be described in terms of a particulate hypothesis.

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† See problem 1.

Atomic Spectra and the Quantum Theory

According to nineteenth-century physics, any accelerating charge should radiate energy. Consequently, if electrons revolved around atomic nuclei, as postulated by Rutherford in 1911, energy should be emitted continuously, since the constant changing of direction in a circular path constituted a normal acceleration. The electrostatic attraction between electron and nucleus provided the force to produce this motion, and it was readily shown that the total energy of the system was greater, the greater the radius of the electron orbit. Because of the continuous radiation of energy, the electron orbit should continuously contract, and the electron should therefore fall into the nucleus. The energy would be emitted as radiation, of frequency equal to that of the electron in its orbit. Since this would also change continuously, as the electron pursued its spiral path to the centre, atoms ought to be unstable entities, radiating light of all frequencies—a continuous spectrum—during their passage to self-destruction! In fact, of course, atoms are perfectly stable, and do not emit radiation unless excited in some way.

One way of producing an emission spectrum is to raise the atoms to a high temperature; this happens, for instance, in a sodium discharge tube, which gives out the familiar yellow light. When this light is examined with a spectrometer, it is found to consist of quite a small number of wavelengths, a limited number of yellow lines being observed. Similarly, when white light is passed through sodium vapour, dark bands in positions corresponding to these yellow lines, are observed in the continuous spectrum of the white light. This is an absorption spectrum of sodium vapour. The frequencies of the lines in the sodium spectrum can all be expressed as the differences between particular pairs of a comparatively small number of quantities, called spectral *terms*. The same is true for the spectra of other atoms.

The inescapable conclusion is that electrons in atoms do not obey the laws of nineteenth-century physics. Electrons in atoms apparently *can* rotate without change of energy, and their total energy can have only a limited set of values.

Bohr's Theory of the Hydrogen Atom

In 1913, Niels Bohr applied the quantum theory to electrons in atoms, choosing the simplest atom, hydrogen. In the theory of the photoelectric effect, it had been postulated that a continuously variable amount of energy could not be absorbed from radiation, but only packets of energy of definite size, the size depending on the frequency of the radiation. In much the same way, Bohr said that the energy of an electron in an atom could not vary continuously, but only by finite amounts. Further, such a variation in the energy of an electron only came about when the electron moved from one orbit to another. On raising the temperature of sodium, for instance, the electrons in some sodium atoms would be raised to orbits of higher energy than usual. They would soon fall back again, and in so doing might emit, as radiation, an amount of energy equal to the difference between that of the two orbits. Since there could be only a finite number of orbits, so also there could be only a finite number of energy quantities emitted and a finite number of spectral lines. Bohr used the Einstein relationship to find the frequency ν of the radiation given out. If the energies of upper and lower orbits were respectively E_1 and E_2, then:

$$E_1 - E_2 = h\nu$$

Plainly, the quantities E/h were to be identified with the experimentally observed spectral terms. Bohr made the arbitrary assumption that the only possible orbits for an electron in a hydrogen atom, were those for which the angular momentum, $mr^2\omega$ (ω being the angular velocity of the electron, m its mass and r the radius of the orbit), was equal to $nh/2\pi$, where n was an