REFERENCE BOOK

of

INORGANIC CHEMISTRY

THIRD EDITION

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REFERENCE BOOK
of Inorganic Chemistry

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PREFACE TO THE THIRD EDITION

In preparing this third edition, we have kept constantly in mind our original objective, a single convenient volume to which the chemist may turn to find the facts or data relevant to the majority of problems which he may encounter. Increased emphasis has been placed upon thermodynamical data, such as oxidation potentials, equilibrium constants and free energies, since they may be used to express so concisely the tendency of a reaction to go, and the nature of the equilibrium state. Oxidation-reduction potential diagrams have now been given for almost every element.

Actinium and the heavier elements have been treated in a new chapter with the title, "The Actinide Elements," and considerable attention has been given to the chemistry of plutonium and the other new transuranium elements. The chapter on the atomic nucleus has been completely rewritten to include all the general types of nuclear reactions. A discussion of nuclear fission and various pile reactors has been added. At the end of this chapter, the table of nuclear properties has been extended to include all known isotopes.

New investigations have been noted in the general field of inorganic chemistry and additions have been made to most chapters, especially those dealing with boron, phosphorus, and silicon. Sections on the chemical industries have been brought up to date, and in many cases, greatly expanded.

The text has not been "written down" to the level of elementary students. A foreign language may be mastered either by starting with a primer or by hearing the language spoken and used in every day life. In the first year chemis-

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try course at the University of California, both methods of teaching the language of chemistry are employed. We believe that, by the end of the year, the students can acquire the facility to read and understand the literature of inorganic chemistry, and that the ability to use the *Reference Book* will be of great value to them in their subsequent professional work.

W. M. L.

BERKELEY, CALIFORNIA
March, 1951

PREFACE TO THE FIRST EDITION

This book represents the fulfillment of a plan, long cherished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

This "Reference Book of Inorganic Chemistry" has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods.

Chemical properties have been widely related to atomic structures and sizes. These ideas, although new, and subject to revision, are so illuminating that they appeal strongly to the imagination. Moreover, they are not difficult to grasp; many concepts traditionally introduced into freshman courses are far more elusive.

The formulas of many compounds have been given in terms of the Lewis theory of valence, not with the idea that these formulas represent the definite locations of the

electrons, but rather to call attention to the importance of considering the total number of electrons or electron pairs in a molecule.

The extensive tabulation of "half reaction" potentials, equivalent to free energy values, will enable one to predict the direction and driving force of an immense number of reactions. Many of these potentials have been calculated for this book from reaction heats and entropy values, and have not heretofore been published.

We have treated industrial processes with emphasis upon their chemistry, relation to other industries, and economic magnitude, rather than upon their mechanical features. Illustrations of industrial processes, of the sort extensively used in some texts, have been left to the instructor to provide, as he can do so far more adequately, by the use of lantern slides and motion pictures. Many excellent films are now available at a nominal expense.

The book contains much more material than the average student, or even the average chemist, can assimilate. We believe, however, that students should be "exposed" to a far greater range of subject matter than is usually presented. We have found the appetite and assimilative capacity of the superior students to be almost unlimited, and we see no value in an intellectual diet list. For the average student, the presence of this extra material in the book does no more damage than the unordered articles listed on a restaurant menu.

We anticipate that this kind of a book will prove useful, not only to the freshman student, but also to the student who desires a reference book in advanced courses in chemistry and allied subjects; and further that teachers and industrial chemists will also find in it answers to many of their questions. To increase its usefulness, a large mass of data has been included in the form of tables, both in the text and in the various appendices.

In the endeavor to keep the size and cost of the book at

a low figure, it was decided to omit references to the original sources of material, although in many instances such references would be of historical and scientific value. Frequent use has been made of the more comprehensive treatises, especially: Gmelin-Kraut's Handbuch der anorganischen Chemie; Abegg and Auerbach Handbuch der anorganischen Chemie; A Text-Book of Inorganic Chemistry, Edited by Friend; A Comprehensive Treatise on Inorganic and Theoretical Chemistry by Mellor; Lexikon der anorganischen Verbindungen by Hoffman; Landolt-Börnstein Tabellen; and The International Critical Tables.

The authors are much indebted to their colleagues in the Department of Chemistry of the University of California, especially to Professors G. N. Lewis and W. C. Bray, not only for specific criticisms and suggestions, but for many of the general ideas upon which our interpretation of the facts of inorganic chemistry has been constructed.

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BERKELEY, CALIFORNIA
December, 1923.

Reference Book of
Inorganic Chemistry

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Appendices

Chapter I

HYDROGEN

1. Structure of Hydrogen Atom.—The element, hydrogen, has three **isotopes,** their mass numbers being one, two, and three. The isotope of mass one is by far the most abundant; the hydrogen of ordinary water contains 0.0156 per cent of the isotope with mass two, and practically none of the isotope with mass three. The latter is formed in certain nuclear reactions but undergoes radioactive decomposition. The mass two isotope is called **deuterium** and the mass three isotope is called **tritium.** It is not customary to designate isotopes by special names, but in this case the percentage difference in the masses greatly exceeds that of any two isotopes of the other elements and there is a correspondingly greater divergence in their physical and chemical properties.

The hydrogen atom (mass one isotope) is composed of two corpuscles; one, the **proton,** is positively charged and the other, the **electron,** is negatively charged. The mass of the proton is about 1,850 times that of the electron but the electrical charges, though opposite in sign, are equal in magnitude.

The atom has a large number of energy states representing different configurations of the electron and proton. The values for the energy of the atom in these different states may be expressed as a close approximation by the very simple relation $E = \dfrac{-13.54Z^2}{N^2}$ volts per unit charge, where

Z is the charge on the proton (equal to unity) and N, called the **quantum number,** is any integer from 1 to ∞. The normal atom is in the first quantum state $(N = 1)$ and the energy in volts required to move the electron to the 2, 3, 4, 5, $\cdots \infty$ quantum states is shown in Fig. 1. When $N = \infty$ the energy is zero. This corresponds to the complete separation of the electron and proton, and the total energy required per unit charge is given as 13.54 volts.
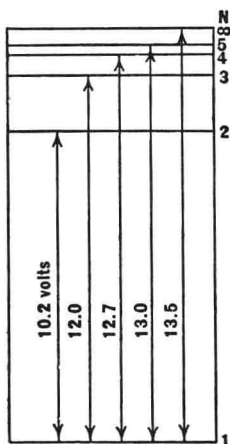

FIG. 1. Energy levels in the hydrogen atom.

When the electron moves from a higher quantum level to a lower, the energy difference is emitted in the form of light, whose frequency, ν, is related to the energy difference, ΔE, by the equation, $\Delta E = h\nu$, where h is a constant ("Planck constant"). Likewise the atom in a lower quantum state may absorb energy in the form of light of a given frequency and the electron thereby move to a quantum level of correspondingly higher energy. The spectral lines arising from electrons falling from outer levels to the first quantum level are far out in the ultraviolet, but transitions from outer levels to the second quantum state give rise to the Balmer series which is in the visible spectrum. The highest frequency in the hydrogen spectrum is, of course, that corresponding to the electron falling from the infinite quantum state.

Bohr has sought to account for these quantum states by picturing the electron as revolving about the proton in some one of a number of possible orbits, which are circles or ellipses. These orbits are defined by the restriction that the momentum of the system must always be some multiple, i.e. the quantum number, of a single fundamental quantity. The total quantum number was considered to be the sum of two other numbers, one giving the units of angular mo-

mentum and the other the units of radial momentum, that is, momentum in the direction of the radius. These numbers fix the size and shape of the orbits. Figure 2 represents these orbits for the total quantum number, $N = 1$, 2, and 3, and the angular momentum as given by the subscripts. The radius of the 1_1 orbit is 0.529×10^{-8} cm.

While the existence of discrete energy states rests upon experimental facts, the Bohr theory has had to be modified

FIG. 2. Electron orbits of hydrogen as pictured by Bohr.

so that the orbits no longer have their former clear-cut meaning. The changes are due to the discovery that some sort of wave motion is associated with a moving particle. This has led to modifications in the equations of motion to give probabilities rather than precise answers. The orbits are now generally referred to as eigen functions, or **orbitals,** from which the probability of finding the electron in a given region may be determined. Figure 3 is a schematic representation of the wave mechanic picture and may be considered as a composite of the electron in many positions to give an average electron density. The electrons are designated as s, p, d, f, $g \cdots$ corresponding to 0, 1, 2, 3, 4 $\cdots$ units of angular momentum.

2. The same general quantum relations as outlined above hold for the other elements, complicated, however, by the facts: (1) that the positive center is no longer a simple unit charge but a complex structure with a net positive charge equal to the atomic number, and (2) that the number of electrons is not one, but a number equal to the atomic number. It is the distribution of these electrons among the various quantum states that determines the grouping of the elements into the so-called "chemical families." The maximum number of electrons in any atom that can have the same total quantum number N is $2N^2$, e.g. for $N = 1$, the
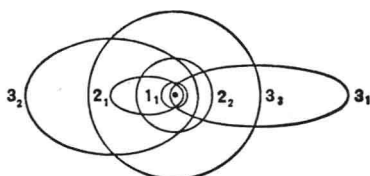
maximum number of electrons is 2; for $N = 2$, it is 8. Hence when the first quantum level is complete with the second element, helium, the three electrons of the third element, lithium, cannot all remain in the first level, but one of them is forced into the second. With each succeeding element of higher atomic number, the number of electrons in the second level increases until it is filled with eight electrons, i.e. in neon. Each alkali metal marks the beginning of a
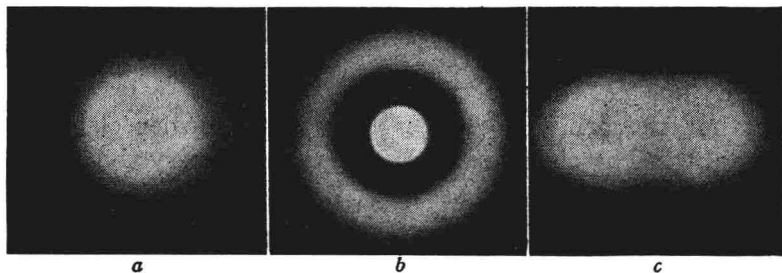

FIG. 3. Different states of the hydrogen atom (after H. E. White): a, the atom with a $1 s$ electron; b, $2 s$ electron; c, one of the states with a $2 p$ electron in a magnetic field.

new quantum group and each noble gas the completion of a group.

Each orbital (Par. 1) contains a maximum of two electrons and the total number of electrons for any one value of the total quantum number, N, and radial quantum number l is $2(2l + 1)$. Thus for the first shell there are two s electrons, for the second two s and six p, for the third, two s, six p, and ten d, and so on. A complete table of the distribution of the electrons in the various atoms is given in Appendix XVIII. The magnetic properties of the electron indicate that it has a quantized spin motion. However when an orbital contains two electrons, the resultant magnetic spin moment is zero, that is, the two spins are in opposite directions.

3. Occurrence of Hydrogen.—Only about one per cent by weight of the earth's crust (outer 10 miles) is hydrogen.

However, if the composition is expressed in terms of the number of atoms, it may be stated that about sixteen per cent of all the atoms on the earth's surface are hydrogen, being second in abundance to oxygen. The major portion of the earth's hydrogen is combined with oxygen in water. It also frequently occurs combined with sulfur, carbon, nitrogen, and chlorine, and less frequently with the other halogens and phosphorus. Hydrogen is a constituent of all acids, and of all animal and vegetable tissue. Only a trace of free hydrogen is found in the atmosphere, but larger quantities are sometimes found in volcanic and other natural gases. Hydrogen appears to constitute 30 per cent of the mass of the sun and spectral analysis of light from the stars indicates that hydrogen is by far the most abundant element in the universe (cf. Append. XIX).

4. Molecular Hydrogen.—Atomic hydrogen combines to form the molecule H_2. Representing the proton by **H,** and the electron by a dot, we may write **H:H** as the electronic formula of the molecule, indicating that the two electrons constitute a bond holding the protons together. Due to the spin of the protons, two forms of the molecule exist: para- with spin directions opposed and ortho- with the spins the same. At room temperature the gas is $\frac{1}{4}$ para- and $\frac{3}{4}$ ortho- in an equilibrium mixture. Equilibrium at the boiling point gives almost pure para- but the change from the high temperature mixture is slow. It is however catalyzed by charcoal and other surfaces. The boiling point of pure para-hydrogen is $20.25°$ K.

Hydrogen has the lowest molecular weight and hence the smallest density of any substance, and, with the exception of helium, the lowest melting point and the lowest boiling point. The gas is odorless, tasteless, and colorless. The most important physical constants are collected in Table I.

Hydrogen was first liquefied by Dewar (1898). The gas in expanding from high pressure to low pressure is