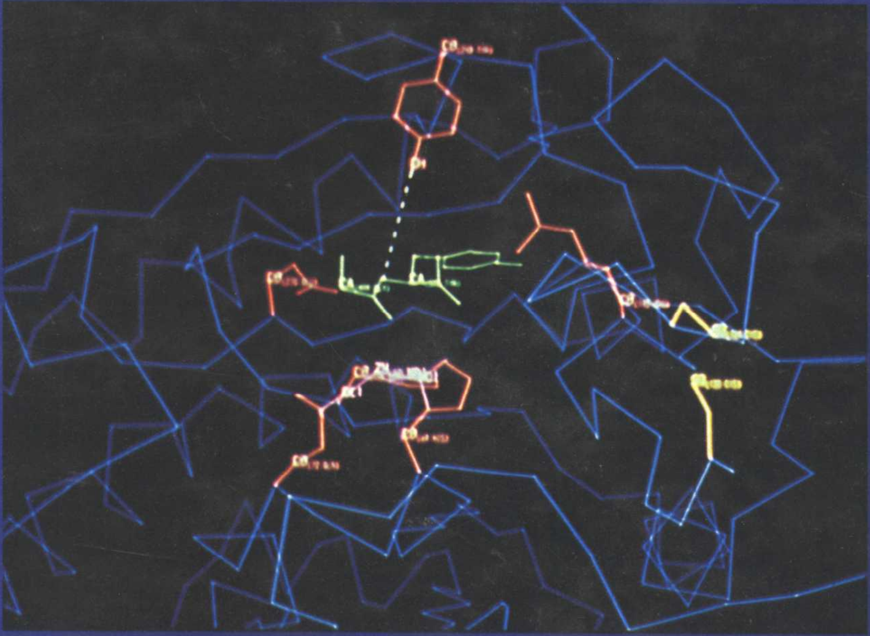
# Concepts and Models of INORGANIC CHEMISTRY



2nd edition

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# INORGANIC CHEMISTRY

## 2ND EDITION

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*Cover illustration:* Computer-generated drawing of Carboxypeptidase A. Color coding: background α-carbon chain, blue; amino acids in the active site, red; zinc and associated atoms, white; cysteine, yellow; and inhibitor, green. (Courtesy of Dr. Robert Langridge, Computer Graphics Laboratory, University of California, San Francisco, © The Regents of the University of California.)

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# Preface

The title of the book still serves as a central theme. The text should help students integrate their knowledge of chemistry, enabling them to draw on the wealth of knowledge learned in the highly compartmentalized chemistry courses. The upper level inorganic course is a fun course for many of us (instructors and students) because here many students gain an overall view of chemistry and acquire the intuitive feel of a chemist. The concepts-and-models approach should foster this goal.

The first edition of this text appeared in 1965. The developments in inorganic chemistry since then have been impressive. We have made the following additions to the text to keep abreast of these developments. We use figures more extensively than in the first edition; they have been selected with care and rendered more effectively. The treatment of bonding is more sophisticated, using molecular orbital theory (Chapter 4). Symmetry and group theory (Chapter 3) are presented for applications to bonding; with this background we are able to have a more detailed discussion of ligand field spectra (Chapter 7). Because the solid state is not given proper emphasis in inorganic courses, discussion of this topic has been expanded (Chapter 6). Reaction mechanisms have increased in importance and receive greater attention (Chapters 9 and 10). The field of organometallic chemistry has grown tremendously and requires a full chapter (Chapter 10), including reaction mechanisms. The treatment of hard and soft acids and bases was added (Chapter 12), and applications to coordination chemistry are included in the same chapter. More descriptive chemistry has been added in Chapters 13, 14, 15, and elsewhere. The importance of the emerging field of metal cluster compounds was acknowledged in the first edition by using a picture of the $Re_3Cl_{12}^{3-}$ structure on the dust jacket, and metal clusters are now recognized to be much more common than had been believed. More systematic treatments of cage and cluster compounds merit regrouping of the topics (Chapter 15). Bioinorganic chemistry (Chapter 16) has become a major component of inorganic chemistry and requires introduction.

The goal of the text is to offer a reasonable balance of material for an upper level undergraduate or first year graduate course. Even reasonable, but not comprehensive, coverage of the currently important topics in inorganic chemistry leads to a book that is too large for a one semester course. Each instructor must select topics and decide on emphasis. Material is provided for courses differing significantly in the balance between theory and descriptive chemistry. Chapters 8, 10, 13, 14, and 15 are primarily descriptive, although in Chapters 6, 9, 11, 12, and 16 we have incorporated a great deal of descriptive chemistry.

Chapter 3 presents symmetry and a brief introduction to group theory for applications to bonding and spectroscopy. The material in Chapters 3, 4, and 7 is organized so that group theory and its applications can be omitted, with the sections using group theory identified.

In a one term course we recommend coverage of the following sections as a basic ''core'': Sections 2.1–2.4, 3.1–3.4, 4.1–4.2, 6.1, 6.3, 7.1–7.5, 9.1–9.3.5, and 12.2–12.3. Beyond this ''core'', these topics can be expanded and others added to satisfy the interests of the instructor and the objectives of the course.

A Solutions Manual is available. It could prove very helpful to students if used properly.

We thank colleagues who have read parts of the manuscript and made useful suggestions, including Rex Shepherd, Darel Straub, and John Thayer. The book was improved by detailed comments on the entire manuscript by Edwin H. Abbott, William E. Hatfield, Duward F. Shriver, and Andrew Wojcicki. Finally, we wish to acknowledge the aid of Marty McDaniel in proofreading.

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# Preface to the First Edition

This book is intended for use as a text in advanced undergraduate courses in inorganic chemistry, with physical chemistry as a prerequisite or at least a corequisite. It is also suitable for a beginning graduate course for students who have not had an advanced undergraduate course. The level of the treatment will stimulate the student to use his preparation in chemistry and physics. An inorganic chemistry course should present the challenge of modern inorganic chemistry and at the same time unify many of the principles and facts presented in earlier courses.

A textbook should serve a number of functions. The first and foremost of these is to acquaint the reader with the theory which undergirds the subject. This is particularly important in chemistry where observations in the laboratory are used to make inferences about the unseen behavior of molecular species. The chemist creates mental models to rationalize the behavior he seeks to describe, and he spends much of his time dealing with these models. A fruitful model serves not only to organize a number of observations, but also as a basis for prediction and to stimulate testing of the model by critical experiments. In this text we present some of the models and concepts of inorganic chemistry in current use. Some are models in the literal sense that they may be visualized and drawings or physical models made, as with shapes of orbitals, while some may not readily be pictured in physical space, as in the case of energy levels.

As well as providing a theoretical base for the subject, a new book in any area should keep the reader up to date. This can be done only if the new ideas appearing in the literature are selectively introduced into the text. Recent topics introduced in this text include crystal field theory, molecular orbitals, boron hydrides, and compounds of the rare gases.

A text should also organize and present effectively ideas which have proven of value for some time. The bases for concepts such as electronegativity and ionic radii are explored here.

The first four chapters present the models and concepts fundamental to inorganic chemistry. Although this book was written with a one-semester course in view, it is not expected that all chapters will necessarily be covered in one semester. Chapters V through XII may be treated as virtually independent topics with material to be selected at the discretion of the instructor. Frequent cross-references are given to facilitate such usage. Many instructors will prefer to refer students to Chapter XII (structural tools), introducing lecture material as needed for other chapters.

Some of the topics within individual chapters are included primarily to serve as a springboard for more advanced courses. For example, the treatment of spectroscopic terms given here provides the left-hand side of an Orgel diagram. The development of the right-hand side may then be carried out in a course in coordination compounds. The brief review of symmetry (Appendix C) and the discussion of the application of symmetry to molecular orbitals (Appendix D) represent extensions, which are becoming increasingly important, of the material in the text. It seemed most appropriate to separate this material from the main body of the text to provide better continuity for those instructors who do not cover this material.

Tables and figures have been used liberally throughout this book. These contain information essential to the portions of the text where they appear and are appropriately indexed. The Appendices and references included in each chapter are intended to extend the usefulness of the book beyond the classroom. It is hoped that the student will find it a useful reference source, which will continue to be of value after he has finished with it as a text.

The authors would like to thank Dr. Elmer Amma for the preparation of a treatment on molecular orbitals, Appendix D, and Dr. Alan Searcy for the example problem on the use of approximation methods in establishing half-cell emf values. We are indebted to our many friends and colleagues who read parts of the manuscript during its preparation and made numerous helpful suggestions. Among these we would like especially to thank Drs. C. H. Brubaker, Jr., T. B. Cameron, J. C. Carter, Joyce Corey, H. S. Frank, H. H. Jaffé, W. L. Jolly, L. N. Mulay, and D. K. Straub. For critically reading the entire manuscript we would like to express our gratitude to Dr. Gordon Atkinson. Finally, we would like to acknowledge the less specific, but no less important, contributions of our teachers and colleagues, who will be aware of their influence in the development of the ideas in this text.

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# 1

# Atomic Structure and the Periodic Table

The periodic trends among elements are the result of the regular pattern in electron configurations of atoms. By examining the early development of the periodic table and the Bohr theory we will see the historical background for our modern views of atomic structure. We will also explore how the results of the wave mechanical description provide the basis for later treatments of bonding and spectroscopy. Here we briefly consider atomic spectra, the derivation of spectroscopic term symbols, and periodic trends for electron configurations and the attraction for electrons (ionization energies and electron affinities).

## 1.1 HISTORICAL BACKGROUND

A systematic approach to inorganic chemistry is today almost synonymous with studying the periodic relationships of the elements and their compounds. This approach has an empirical foundation built during the last century and a theoretical justification of half a century.

Within a decade following the presentation of a consistent set of atomic weights by Stanislao Cannizzaro at the Karlsruhe Conference in 1860, various forms of the periodic table appeared in France, England, Germany, and Russia. The role played by Cannizzaro's list of atomic weights in the development of the periodic table can better be appreciated by recalling that an attempt in 1852 by Gladstone to find a relationship between the atomic weights and other properties of the elements failed, because of the lack of a consistent set of atomic weights. The greatest share of credit for the periodic table is usually given to Dimitri Mendeleyev, and properly so, for it was the realization of his bold prophecy of new elements and their properties that led to the almost immediate acceptance of the periodic law. In 1871, Mendeleyev made the following predictions about an element that was discovered by Boisbaudran in 1875.

> The properties of ekaaluminum, according to the periodic law, should be the following: Its atomic weight will be 68. Its oxide will have the formula $El_2O_3$; its salts will present the formula $ElX_3$. Thus, for example, the chloride of ekaaluminum will be $ElCl_3$; it will give for analysis 39% metal and 61% chlorine and will be more volatile than $ZnCl_2$. The sulfide $El_2S_3$, or oxysulfide $El_2(S,O)_3$, will be precipitated by $H_2S$ and will be insoluble in ammonium sulfide. The metal will be easily obtained by reduction; its density will be 5.9, accordingly its atomic volume will be 11.5; it will be soft, and fusible at a very low temperature. It will not be oxidized on contact with air; it will decompose water when heated to redness. The pure liquid metal will not be attacked by acids and only slowly by alkali. The oxide $El_2O_3$ will have a specific gravity of approximately 5.5; it should be soluble in strong acids, forming an amorphous hydrate insoluble in water, dissolving in acids and alkali. The oxide of ekaaluminum will form the neutral salts and basic $El_2(OH,X)_6$, but no acid salts; the alum $KEl(SO_4)_2 \cdot 12H_2O$ will be more soluble than the corresponding salt of aluminum and less crystallizable. The basic properties of $El_2O_3$ being more pronounced than those of $Al_2O_3$ and less than that of ZnO . . . it will be precipitated by barium carbonate. The volatility as well as the other properties of the salts of ekaaluminum will be a mean between those of Al and In. It is probable that the metal in question will be discovered by spectral analysis as have been In and Tl.

Examining the above predicted properties for gallium reveals some properties that vary systematically with the position of the element in the periodic table—physical properties of the element and its compounds (specific gravity, hardness, melting point, boiling point, etc.), spectrographic properties, and chemical properties (formulas of possible compounds, acidic and basic properties of compounds, etc.). In fact, properties of the elements or their compounds that cannot be correlated by means of the periodic table are somewhat exceptional.[1]

Much of this book is devoted to attempting to understand the underlying principles that bring about these periodic relationships: that is, properties that show greater than average similarity for elements which lie in the periodic table (a) in a vertical column (called a group), (b) in a horizontal row (called a period), (c) within a given area (bounded by elements of two or more groups and two or more periods), and (d) on diagonals. The following illustrate these types of relationships. Elements in a group have similar arc and spark spectra; often, similar valences; similar crystal structures both for the element and for particular series of compounds, etc. Elements in a given period have similar maximum coordination numbers in their compounds. The compounds of the second-period elements Li, Be, and B show many similarities to the compounds of the third-period elements Mg, Al, and Si, to which they are diagonally related. Finally, there are numerous properties, such as classification of the elements as metals, metalloids, and nonmetals, that have an area relationship to the periodic table. The area relationships are often the most difficult to explain, because of the wider possible variation of the factors involved. Thus it may be difficult to explain in an *a priori* fashion why the carbides

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[1] One of the major classes of "exceptional" properties is nuclear properties—nuclear magnetic moments, isotopic abundance, etc. These properties, however, may be rationalized on the basis of a "shell theory of the nucleus," which is analogous to the theoretical justification of the chemical periodic table. See B. H. Flowers, *J. Chem. Educ.* 1960, *37*, 610. Maria Goeppert Mayer won the Nobel Prize in Physics in 1963 for this theory; for her Nobel address, see *Angew. Chem.* 1964, *76*, 729.

of a given area are explosive—but that is certainly worthwhile knowing if you contemplate making carbides or acetylides of elements lying in or near such a known area.

Before proceeding to the theoretical basis of the periodic table, let us note the following steps in its evolution.

By 1829, Döbereiner had pointed out that there were a number of cases in which three elements, or triads, have similar chemical properties; and further, that one member of a triad has properties very close to the mean value of the other two—this is particularly true of the atomic weights.

Between 1860 and 1870, Newland, Meyer, and Mendeleyev prepared periodic tables by listing the elements in the order of increasing atomic weights and then grouping them according to chemical properties. In Mendeleyev's table the triads of Döbereiner always fell within the same group. It may, at first, appear odd that for the group VIII elements more than one element is listed in a period, but the elements iron, cobalt, and nickel form one of Döbereiner's triads and hence have to appear in the same group. Mendeleyev reassigned atomic weights to a number of elements in order to obtain a fit with the chemical properties of the other elements in the group. Later evaluations confirmed the need for reordering the atomic weights of some of the elements but firmly established a reversal in atomic weights, as compared to the position in the periodic table, for several pairs of elements (Te and I, Co and Ni are the early known cases.)

As the rare earth elements were discovered, difficulty was encountered in fitting them in the table. This led Basset and later Thomsen to propose the extended form of the table generally accepted today (see Figure 1.1.) Further, from considering the change of group valence from $-1$ for the halogens to $+1$ for the alkali metals, Thomsen reasoned that one should expect a group of elements lying between groups VII and I and having either infinite or zero valence. Since a valence of infinity is unacceptable from a chemical viewpoint, he proposed that a group of elements of zero valence separated the highly electronegative halogens from the highly electropositive alkali metals. He proceeded to predict the atomic weights of these elements as 4, 20, 36, 84, 132, and 212. He felt that these elements should terminate each period. Unfortunately, Thomsen did not publish these remarkable predictions until after argon had been discovered.

The last stage in the empirical development of the periodic table came in 1913, when Moseley found the x-ray emission from different elements had characteristic frequencies ($\nu$), which varied in a regular fashion with the ordinal number of the elements as they appear in the table. The empirical relationship is

$$\nu = k(Z - \sigma)^2 \tag{1.1}$$

where $Z$ is the ordinal or atomic number, $\nu$ is the characteristic x-ray frequency, and $k$ and $\sigma$ are constants for a given series. No reversals in atomic number occur in the periodic table; hence, it is a more fundamental property of an element than the atomic weight.

The empirical evolution of the periodic table had reached its peak. It was now possible to make a strictly ordered list of the elements with definite indication of missing elements. Each period terminated with a noble gas and it was possible to tell how many elements belonged to each period.

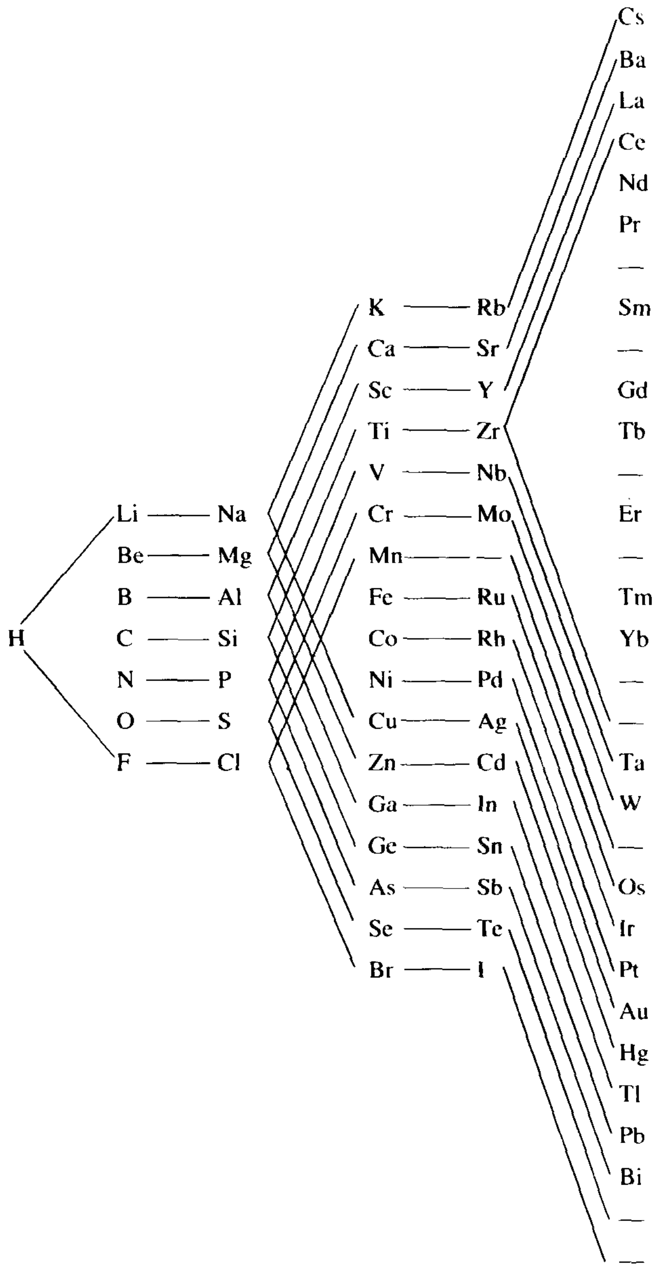

**Figure 1.1** Long form of periodic table. (Proposed by J. Thomsen, *Z. Anorg. Chem.* 1895, 9, 190.)

## 1.2 ATOMIC STRUCTURE AND THE THEORETICAL BASIS OF THE PERIODIC TABLE

The theoretical basis of the periodic table had to await the development of a clearer picture of the atom. The concept of atoms as fundamental or indivisible particles had to be abandoned at the beginning of this century. Studies of cathode rays and canal rays led to the recognition of the existence of negative and positive charges within the atom. Further complexity of the atom could be inferred from emission spectra of gaseous substances in magnetic fields (the Zeeman effect) and the discovery of radioactivity. Radioactivity not only indicated that the atom was not a fundamental unit, but also provided a probe with which to examine the atom. From the scattering of alpha particles by thin metal foils, Rutherford arrived at a nuclear model of the atom, with a nucleus carrying a number of unit charges equal to approximately one half the atomic weight of the element. Van den Brock pointed out that the use of the ordinal number of the element in the periodic table—that is, the atomic number—for the number of unit charges on the nucleus improved the fit of the alpha scattering data. Moseley also associated the atomic number with the nuclear charge.

## 1.2.1 Bohr Model of the Atom

A major advance in the understanding of the atom was Niels Bohr's development of a model of the atom that could account for the spectra of hydrogenlike atoms (i.e., one electron, one nucleus—H, $He^+$, $Li^{2+}$, etc.). In developing his model Bohr accepted some past notions, rejected others, and assumed some new ones.

1. The Rutherford nuclear model of the atom was accepted.
2. The theories of Planck and of Einstein that radiant energy is quantized in units of $h\nu$, where $h$ is Planck's constant and $\nu$ is the frequency of the radiant energy, were accepted.
3. The classical electrodynamic theory that a charged particle undergoing acceleration must emit electromagnetic radiation was rejected for electrons within atoms.
4. The electron was assumed to travel in circular orbits.
5. Of all possible orbits, only those for which the electron had a specified angular momentum were acceptable (that is, the angular momentum was quantized).
6. It was postulated that radiation was emitted or absorbed only when the electron jumped from one orbit to another, the energy emitted or absorbed corresponding to the difference in the energies for the initial and final states of the system.
7. Except as noted above, classical physics was assumed to be applicable to the atom.

Before going further, we should note that Bohr's assumption of circular orbits has been shown to be much too restrictive. Assumptions **1, 2, 3,** and **6** are retained in wave mechanics, whereas **5** comes as a result of the one arbitrary assumption of wave mechanics. Accordingly, we will not pay too much attention to the geometry of the Bohr model, but rather shall be more concerned with the energy states of the atom based on Bohr's model.

From **1** and **4** above, the Bohr model for hydrogenlike atoms may be pictured as having a heavy nucleus bearing a charge of $Ze$ (where $Z$ is the atomic number and $e$ is the magnitude of the charge on the electron) with an electron of charge $e$ and mass $m$ traveling with a velocity $v$ in an orbit of radius $r$ from the nucleus (See Figure 1.2.)

The following relationships result from the assumptions listed above.

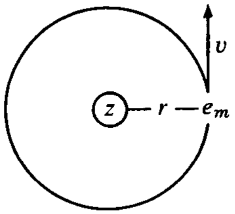

**Figure 1.2** Bohr model of hydrogenlike atoms.

From classical physics (7) the centrifugal force may be equated with the coulombic attraction

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \tag{1.2}$$

or

$$mv^2r = Ze^2 \tag{1.3}$$

The total energy, $E$, is the sum of the kinetic and potential energy

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} \tag{1.4}$$

substituting from (1.2) for $\frac{1}{2}mv^2$

$$E = -\frac{1}{2}\frac{Ze^2}{r} \tag{1.5}$$

Quantizing the angular momentum

$$mvr = n\left(\frac{h}{2\pi}\right) \tag{1.6}$$

where $n$ (called the quantum number) must be an integer and $h$ is Planck's constant.

From (1.2) ÷ (1.6)

$$v = Ze^2\frac{2\pi}{nh} \tag{1.7}$$

From (1.3) and (1.7)

$$r = \frac{Ze^2}{mv^2} = \frac{n^2h^2}{4\pi^2mZe^2} \tag{1.8}$$

From (1.5) and (1.8)

$$E = -\frac{2\pi^2mZ^2e^4}{n^2h^2} = \frac{E_{(n=1)}}{n^2} \tag{1.9}$$

This equation gives the energy of hydrogenlike atoms in various quantum states. For the hydrogen atom itself, the lowest energy state—that is, the quantum state for $n = 1$—has the value of $-13.6$ eV or $-1312$ kJ/mole. The lowest energy state for an atom (or ion or molecule) is called the *ground state*. The first higher energy state above the ground state is called the