INORGANIC CHEMISTRY

PURCELL AND KOTZ

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PREFACE

One of the problems facing the instructor of inorganic chemistry—and the authors of inorganic textbooks—is the antiquated view that a single semester of three lectures per week will suffice to cover the subject with any degree of thoroughness. This is an outrageously difficult situation, even if it were not for the awesome growth of the field in recent years. Because of this situation, inorganic texts of the past have tended to follow one or the other of two philosophies: to enumerate chemical facts without developing for the student the beauty of their systematics; or, to select a few "topics" for a more detailed examination. Our experience has been that both philosophies fail to give a student a sense of the integrity and continuity of inorganic chemistry. Our effort to write about inorganic chemistry at the senior/graduate interface arose from the frustrations of our students in dealing with such organizational schemes. Too often we found that our students simply developed an attitude of survival. A more serious consequence of this was that the student left the encounter with inorganic chemistry feeling that the field was not systematized; in his view, inorganic chemists must be a disorganized group of specialists largely ignoring each other. Does one have to be a transition metal chemist, *or* a rare gas chemist, *or* a boron chemist? Without an integrated view, the student often missed the excitement and challenge of inorganic chemistry and the almost limitless potential for new discoveries in this field.

Another view that we have developed over the past decade of teaching inorganic chemistry is that the usual senior course uniquely challenges the student to integrate concepts from thermodynamics, kinetics, and bonding theory for their application to chemistry at large. We have written this text in the hope of presenting inorganic chemistry as a focus of many of the concepts our students have previously learned.

The degree to which each of us can realize such goals depends, of course, on our skill as instructors but is limited by the fact that most of us labor under the yoke of approximately forty-five lectures to make our case. *It is not possible to cover all of the material in a text of this size in a semester of the usual length;* we certainly do not do so in our own courses, nor do we advocate that others try. Rather, our attempt to resolve the dilemma is to recognize that each of us will skimp on some aspects and delve more deeply into others. What we have attempted to do, therefore, is to write a text that allows the instructor the flexibility to pursue his convictions on the topics to be stressed and, at the same time, aids the student in integrating those topics. It is our hope that the student is spared the frustrations of an otherwise dislocated treatment of chemistry. Specifically, when a principle or "fact" is encountered we make an effort to note its previous and later use, if these are not obvious.

In other words, we intend to remind the student of what he has seen before and where he will see it again. With the material integrated in this manner, the systematics should develop with little effort on the student's part; equally important, the tentatively non-systematic facts, which are harbingers of new principles, stand out in relief.

At the crudest level of organization, this text is structured into theoretical, non-metal, and metal topics and, in this regard, it is more or less standard. Students often have difficulty with the first of these (bonding treatments) because, while of intrinsic interest, the concepts are soon forgotten by authors in succeeding descriptive sections. We have avoided this because theory without application to observed phenomena is as lifeless as phenomena without a basis for their interpretation. The first four chapters develop theoretical concepts *and their chemical interpretations*. Ultimately, our desire for a unified electronic theory has led us to emphasize *the molecular orbital model,* rather than the myriad approximations to it.

The descriptive non-metal chemistry begins with a chapter on the Lewis donor/acceptor concept and solvent properties for they, along with the structure and bonding concepts of the first four chapters, provide the foundation for the rest of the text. This is followed by two chapters which examine main group structures and reactivities in terms of thermodynamic and mechanistic principles. The second of these (Chapter 7) is especially important since a considerable amount of inorganic chemistry can be organized around mechanistic types, and this book reflects throughout our feeling that mechanisms should be emphasized more strongly.

The descriptive chemistry encountered under the aegis of the more physical aspects of inorganic chemistry is brought to practical focus through the systematic synthesis of non-metal compounds in Chapter 8. Again, this reflects our belief that theory is given special meaning through understanding of, and interest in, the purposeful synthesis of molecules. While Chapter 8 overtly addresses this point, in fact we have attempted to emphasize the synthetic aspects of inorganic chemistry throughout.

The bonding concepts used for non-metal compounds are extended to interpret the special magnetic and electronic properties of *transition metal complexes* in Chapter 9, and Chapters 10 and 11 are devoted to the topologies and stereochemistries of this class of compounds. It is here that the angular overlap model (AOM), a molecular orbital approach, is first brought into use. Although the AOM has been used in the chemical literature, this text is its first use in such a manner that the average undergraduate can cope with the theory. Although the model is as useful as the ligand field model in interpreting spectral and magnetic properties of coordination complexes, the AOM approach finds its greatest use in predicting and interpreting the structural problems in coordination chemistry. It is the only approach of which we are aware that allows a student to assess, in a simple and straightforward manner, the electronic energy bias toward a favored structure of a transition metal coordination complex.

Following these chapters on bonding and structural theory for coordination complexes, there are chapters on the reactions of such compounds. Our approach has been to start "within" the complex to look at electron transfer between metal ions and work outward to reactions of coordinated ligands. Each of these reactivity chapters continues the thermodynamic, kinetic, synthetic sequence of the non-metal chapters and each culminates in an application of the principles developed therein to the synthesis of coordination complexes.

Two additional chapters on metal chemistry—organometallic chemistry—follow. The average undergraduate gains little exposure in his other courses to this very important and rapidly expanding field. It is our belief that most students need some knowledge of organometallic chemistry, and most are intrinsically interested in such material. Organometallic chemistry is developed here along the same lines as the previous chapters on metal chemistry, again with an emphasis on reaction mechanisms.

The final two chapters describe two other expanding areas of inorganic chemistry: metal and non-metal cluster chemistry and inorganic aspects of biochemistry. Both are areas of considerable importance, and we have treated both within the framework of the structural and bonding principles laid down in the earlier chapters. (The topic of polyhedral boron hydrides received recent recognition by the announcement that Professor W. N. Lipscomb was awarded the 1976 Nobel Prize in Chemistry for his pioneering work on the bonding in such compounds.) Finally, the chapter on inorganic biochemistry is perhaps different from other published approaches in that, rather than simply recounting inorganic prosthetic groups, a synopsis is given of the bio-processes in which such reagents are necessary.

We are greatly indebted to our reviewers (Mike Bellema, Bob Fay, Ron Gillespie, Bill Hatfield, Galen Stuckey, and Jerry Zuckerman) for critically examining the manuscript and insisting on clarity of presentation and accuracy of facts. Some of our students and faculty colleagues (especially Tay Tahk and Bruce Knauer) have generously given time and effort to the improvement of this text; to all of them we are sincerely grateful. The editors and artists of W. B. Saunders Company and York Graphic Services have done an outstanding job in bringing this project to its conclusion. John Vondeling gave support beyond what is customary from editors in such endeavors and Jay Freedman time and again proved an invaluable partner. Finally, to our wives, Susan and Katie, and to our children (Kristan and Karen, David and Peter) go our deepest appreciation and thanks, as well as a promise; there will be more time now for sailing/backpacking and evenings at home.

K. F. PURCELL

J. C. KOTZ

A NOTE ON UNITS

After much soul searching, and in view of the primarily American usage of this text, your authors have opted to use the existing hodge-podge of units to which you are accustomed. Inside the front cover you will find a table of units and constants in the SI (Système International d'Unités)[1] and the conversion relations between these and the traditional units used in this text. You would be well advised to learn to use the SI units (they derive from the rationalized MKS units used in physics texts). Current research journals in Britain and on the Continent are using the SI exclusively, and it is beginning to appear in the American research journals as well. The advantages of a standardized system of units are obvious; the reluctance of research scientists to universally adopt them stems from the adoption of units convenient for the phenomena, and instruments, of their studies. For example, the convenient calorimetry unit is the calorie, ionization potential and electrochemical measurements are traditionally reported in electron volts, while the spectroscopist, using Einstein's photoelectric equation, prefers the erg unit.

[1] Probably the most readily accessible material, with applications, is to be found in articles by A. C. Norris, *J. Chem. Educ.*, **48**, 797 (1971); (for magnetic units) T. I. Quickenden and R. C. Marshall, *ibid.*, **49**, 114 (1972) and J. I. Hoppeé, *ibid.*, **49**, 505 (1972); and N. H. Davies, *Chem. Britain*, **6**, 344 (1970); *ibid.*, **7**, 331 (1971). Corrections to the latter papers are to be found in *ibid.*, **8**, 36 (1972).

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