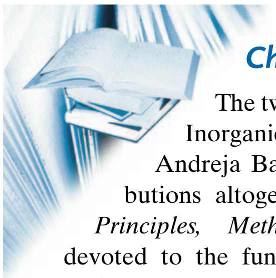
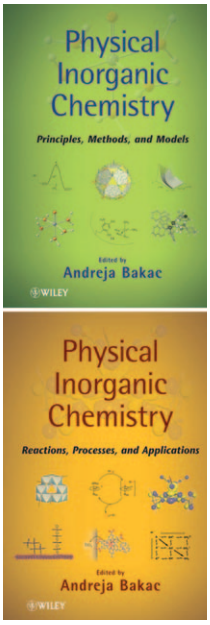


Physical Inorganic Chemistry

The two-volume work Physical Inorganic Chemistry, edited by Andreja Bakac, contains 22 contributions altogether. The first volume, *Principles, Methods, and Models*, is devoted to the fundamentals, whereas the second one, *Reactions, Processes, and Applications*, is concerned with different kinds of chemical reactions.

The chosen title, *Physical Inorganic Chemistry*, could in principle be understood in either of two senses. The first possible approach consists of describing the analytical methods of physical inorganic chemistry and discussing on that basis its applications to inorganic questions. A book that provides a general treatment of the physical chemical aspects of inorganic chemistry is expected to be a complement to standard textbooks of physical chemistry, by beginning where standard textbooks end. In particular, the treatment of methods and techniques and the underlying theory should be continued and deepened, and the examples should come from the area of inorganic chemistry. This approach incurs the risk that technical details and theory will predominate, with inorganic chemistry playing only a minor role. The second possible interpretation consists of defining the most important areas of research within physical inorganic chemistry and then treating them in greater depth. The editor has opted for a not entirely happy blend of the two approaches.

The introduction to the first volume defines the following goal: “It is the goal of this book to present in one place the key features, methods, tools, and techniques of physical inorganic chemistry, to provide examples where this chemistry has produced a major contribution to multidisciplinary efforts, and to point out the possibilities and opportunities for the future.” The following sentence amplifies that by stressing that standard methods are not covered despite their enormous relevance. However, the introduction does not mention that both volumes are devoted almost exclusively to molecular chemistry. Solid state chemistry is touched on, if at all, only marginally. Neither standard nor special methods of solid state chemistry are treated. Moreover, the contributions are mainly concerned with transition-metal chemistry. Compounds of main-group elements are treated only very briefly, despite their topicality. Therefore, the title should more accurately read “Physical Molecular Transition Metal Chemistry”. A further major drawback is that concepts of bonding in clusters or subvalent molecular compounds with metal–metal bonds are not covered.



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The individual articles of the first volume can be divided (more or less accurately) into three classes, although of course the boundaries are diffuse. The first class consists of contributions that introduce a method (or a group of methods), explain the corresponding theory in considerable detail, and supplement it by examples. Secondly come contributions that introduce a particular method, but give only a cursory introduction to the theory, and mainly demonstrate by means of examples what information can be obtained by that method. The majority of the contributions belong to this category. Thirdly, there are contributions that largely omit the presentation of the methodology and essentially limit themselves to delivering (more or less) a list of results.

Chapters 6 and 7 belong to “Class 1”. In Chapter 6, G. Ferraudi presents the theory of flash photolysis (to investigate excited states) in detail, gives an introduction to the experimental technique, and describes many examples of applications. In Chapter 7, C. D. Hubbard and R. van Eldik give an introduction to the pressure dependence of chemical reaction kinetics, describe typical experimental setups, and present some examples, which they discuss in detail.

The second class includes most of the contributions. Chapter 1 (E. I. Solomon and C. B. Bell III) deals with the spectroscopy of electronic transitions. The information that can be obtained from different types of spectra is described and explained by means of a few well-selected examples involving copper and iron complexes. Chapter 2 (M. Marthinho and E. Münck) introduces Mössbauer spectroscopy. A description of the theoretical foundations is followed by some detailed examples concerned especially with complexes of iron in high oxidation states. Chapter 3 (P. Kögerler) deals with magnetic properties. A short introduction to the theory of magnetic properties of matter and a description of the main experimental methods is followed by a few selected examples (single-molecule magnets, oxide cluster compounds). Chapter 5 (J. P. Riehl and S. Kaizaki) gives a somewhat long-winded introduction to the different kinds of chirality and describes methods for determining absolute configurations, with many examples, starting with classical Werner coordination compounds. Isotope effects on rate constants and equilibrium constants are the topic of Chapter 9 (J. P. Roth), taking as examples dioxygen complexes of iron, iridium, and copper. The methodology for measuring the isotope effect of oxygen is presented and examples of applications are given. Chapter 10 (J. N. Harvey) on the calculation of reactivities in transition-metal chemistry gives an overview of different quantum-chemical methods, followed by detailed examples [change of hapticity of cyclooctatetraene complexes, weak interactions (metal–

$H(\delta-)\cdots H(\delta+)$ contacts and agostic interactions)]. The discussion about the question of a computational proof of a mechanism is very instructive. The helpful list (at the end of the chapter) of points that should be taken into consideration in theoretical investigations deserves special praise.

The third class contains two contributions. Chapter 8 (A. Bakac) considers reaction kinetics from the viewpoint of the determination of reaction mechanisms. Different rate laws are explained using examples. The lack of a section about the experimental technique is no drawback here, since it can be assumed that it is based on standard kinetic experiments. The topic of Chapter 4 (I. G. Denisov) is cryo-radiolysis. The section is a mere list of investigations performed. A few examples, worked out in detail, would have been much better.

The second volume is concerned with typical reactions in 12 contributions that are related to the themes solar energy, hydrogen energy, bio-renewables, catalysis, environment, atmosphere, and human health. Chapter 1 (O. Snir and I. A. Weinstock) is different from the rest, as it contains an introduction to a theory, the Marcus theory of electron transfer processes, complemented by a guide to practical applications of the theory. All the other chapters focus on results of investigations. Chapter 2, by S. Fukuzumi, deals with mechanistic questions about oxidative cleavage of C–H bonds, especially with distinguishing between the mechanisms of concerted hydrogen transfer, sequential electron and proton transfer, and hydride transfer. Chapter 3 (M. M. Abu-Omar) is concerned with oxygen atom transfer, and discusses typical (biological and non-biological) oxygen-atom transfer reactions. Chapter 4 (E. V. Rybak-Akimova) deals with the activation of O_2 and bonding to mono- and dinuclear transition-metal complexes. Unfortunately, the discussion of the bonding modes makes no reference to some important benchmark matrix isolation studies. In Chapter 5, G. J. Kubas and D. M. Heinekey discuss the activation of H_2 with transition-metal compounds and describe different methods for the characterization of such complexes. In Chapter 6, F. Joó discusses the activation of carbon dioxide, and reviews the use of CO_2 in various syntheses. Chapter 7 (J. A. Olabe) is concerned with nitrogen monoxide bonded to complexes. The author describes the use of spectroscopic methods for characterization of the complexes and investigation of reaction kinetics. In Chapter 8, T. W. Swaddle discusses the mechanism of ligand substitution in metal complexes. Chapter 9 (D. M. Stanbury) is concerned with the reactivity of inorganic free radicals (including that in aqueous solution). A classification under 15 reaction types is described. Chapter 10 (T. Kégl, G. C. Fortman, M. Temprado, and C. D. Hoff) is concerned with organometallic free radicals. The reactivities of typical examples are discussed. The topic of Chapter 11 (T. B. Gunnoe) is the metal-mediated activation of C–H bonds, with a discussion about different mechanisms. The topic of Chapter 12 (G. J. Meyer) is solar photochemistry using transition metals. It is concerned almost exclusively with the mechanism of charge separation in ruthenium-sensitized TiO_2.

To summarize, the two volumes are rather heterogeneous because of the differences in approach between the chapters. In contrast to what one expects from the very general title *Physical Inorganic Chemistry*, the work is mainly restricted to molecular transition-metal compounds. Main-group chemistry only plays a minor role, except for Chapter 9 of the second volume (free radicals in aqueous solution) and parts of Chapter 8 of the first volume. Solid state chemistry is hardly treated at all. Moreover, some important modern methods of molecular transition-metal chemistry are treated only marginally. For example, vibrational spectroscopy is not adequately covered. The first volume does not have a chapter on vibrational spectroscopy methods, and they only play a significant part in Chapter 5 of the second volume (H_2 complexes) and in Chapter 7 (complexes with NO).

However, despite these limitations the work is a valuable new resource for chemists working in the field of molecular transition-metal chemistry. For everyone who plans to become involved with flash photolysis, with the pressure dependence of chemical reactions, or with the Marcus theory, the work provides instructive introductions. It is also of interest for readers who wish to learn about what kinds of information can be obtained by electronic spectroscopy, Mössbauer spectroscopy, and magnetic investigations, and for those concerned with a computational treatment of reactivity. Furthermore, the great strength of the work is in the wealth of beautifully explained examples.

Olaf Hübner, Hans-Jörg Himmel
Anorganisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg (Germany)

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