Preface to the Second Edition

Over the last decade, since the first edition of *The Chemistry of Superheavy Elements* appeared in 2003, the field of superheavy elements—chemistry and physics, experiment and theory—has made an enormously big leap forward. The discovery of elements 114 and 116, located in the center region of the long sought and highly desired "traditional" Island of Stability, was officially accepted and they were named flerovium (Fl) and livermorium (Lv). Further experiments provide strong evidence for the synthesis of all elements up to atomic number 118; a homolog of radon. With the complete filling of the seventh row of the Periodic Table of the Elements, experimenters set out to search for elements 119 and 120. They will be the first two elements of the eighth period followed by element 121, which would mark the beginning of the super-actinides. Technical advancements enable the beginning of a detailed nuclear spectroscopy of the first transactinides shedding more light on the nuclear structure and stability, including the shell effects, of these elusive elements. This helps to determine the position and strength of those nuclear shells which enable the existence of superheavy elements.

Chemistry has finally reached and is presently focusing on element 114. In addition, a new field of superheavy element chemistry has opened up entirely new perspectives—chemical studies after preseparation with gas-filled recoil separators. This includes metal-organic chemistry of superheavy elements and, potentially, aqueous phase chemistry beyond seaborgium. While advancements in fully-relativistic theoretical chemistry facilitate a much deeper understanding of experimental results, at the same time, experiments also challenge theory.

These are good reasons for an up-to-date second edition of this book. The first chapter of the previous edition was replaced by two completely new and much more extended ones highlighting the nuclear aspects much more than in the first edition.

Chapter 1 deals with nuclear synthesis of superheavy elements, including many production, separation, and identification aspects, and with the nuclear decay properties of the heaviest nuclides. Now, this chapter is focused much more on those nuclear reactions, which recently facilitated the production of the heaviest elements and the more neutron-rich, longer-lived isotopes that are essential for chemical studies.

Chapter 2 outlines the present status of nuclear spectroscopy and nuclear structure studies in the transition region from heavy actinides into transactinides. It includes a detailed discussion of state-of-the-art techniques, provides basic nuclear structure and nuclear model information, as well as recent experimental results.

Chapter 3, which provides a summary of chemical properties of transactinides from a theoretical point of view, is significantly extended over the first edition. This reflects spectacular developments in relativistic quantum theory and computational algorithms, which provide improved information on atomic, ionic, and molecular properties of superheavy elements. It clearly demonstrates the importance of relativistic effects in the chemistry of superheavy elements and enables deeper insights into the architecture of the Periodic Table at its far end.

Chapter 4 discusses fundamental questions of the validity of chemical information obtained one atom-at-a-time. While still presenting concepts of statistical thermodynamics and fluctuation theory, and discussing limitations of atom-at-a-time chemistry, the revised version of this chapter includes a discussion of atom-at-a-time chemistry in more general terms.

Chapter 5 shows the progress made in experimental techniques including automated devices for chemical separations performed in the aqueous phase and the gas-phase as well as coupling of such devices to recoil separators.

Chapter 6 presents the wealth of information obtained about properties of transactinides up to element 106, seaborgium, in the aqueous phase. This includes new and detailed information on the chemistry of elements 104, rutherfordium, and element 105, dubnium.

As in the first edition, the revised version of Chap. 7 discusses thermodynamic data derived from gas-phase adsorption experiments and extrapolations into unknown regions including predictions of thermochemical properties.

Chapter 8 summarizes the results of chemical studies of superheavy elements in the gas-phase and their wall-adsorption properties. In addition to new results on lighter transactinides, first results on gas-phase and wall-adsorption properties of elements 112 and 114 are part of the focus of this chapter. It also provides new information on element 108, hassium, including interesting new nuclear data obtained with chemical methods.

The historical reminiscences of Chap. 9 are completed by one section bridging the gap between early attempts to synthesize superheavy elements and the success of recent experiments.

It is a great pleasure for me to thank my Coeditor Dawn Shaughnessy, who triggered this second edition and worked on many chapters and aspects, and Elizabeth Hawkins from Springer, who not only convinced me to again embark on this enterprise but helped me with her competence and friendliness most patiently through the process of making this edition possible. Many thanks go to the Authors of the individual chapters—the ones who already contributed to the first edition and again worked hard on the second one and the new Authors who helped to widen and deepen many perspectives in this book and bring it up-to-date. Last but

not least it is a great pleasure to again thank Brigitta Schausten for helping technically to get the project started and for her work on some graphics, especially the Periodic Table as a ball.

Wiesbaden, March 2013 Matthias Schädel

Preface to the First Edition

This book is the first to treat the chemistry of superheavy elements, including important related nuclear aspects, as a self contained topic. It is written for those—students and novices—who begin to work and those who are working in this fascinating and challenging field of the heaviest and superheavy elements, for their lecturers, their advisers and for the practicing scientists in the field—chemists and physicists—as the most complete source of reference about our today's knowledge of the chemistry of transactinides and superheavy elements. However, besides a number of very detailed discussions for the experts this book shall also provide interesting and easy to read material for teachers who are interested in this subject, for those chemists and physicists who are not experts in the field and for our interested fellow scientists in adjacent fields. Special emphasis is laid on an extensive coverage of the original literature in the reference part of each of the eight chapters to facilitate further and deeper studies of specific aspects. The index for each chapter should provide help to easily find a desired topic and to use this book as a convenient source to get fast access to a desired topic.

Superheavy elements—chemical elements which are much heavier than those which we know of from our daily life—are a persistent dream in human minds and the kernel of science fiction literature for about a century. This book describes in Chap. 1 how today this dream becomes true at a few accelerator laboratories, what the tools are to synthesize these elusive, man-made elements in heavy-ion nuclear reactions and how to detect the specific nuclear decays which terminate their existence shortly after they are created. The current status of experimental and theoretical insights into this very unique region of nuclear stability is briefly reviewed. The last chapter outlines historical developments, from first scientifically sound ideas about the existence of superheavy elements, which surfaced during the mid-50s, all the way to the beginning of the current research programs described in Chap. 1. It also discusses experimental attempts and prospects of the search for superheavy elements in Nature.

Today, one century after Ernest Rutherford and Frederick Soddy postulated that in the radioactive decay one chemical element transmutes into a new one, we know of 112 chemical elements. The discoveries of elements 114 and 116 are currently waiting to be confirmed and experimentalists are embarking to discover new and heavier elements. Now where are superheavy elements located on a physicist's chart of nuclides and on the Periodic Table of the Elements—the most basic chart in chemistry?

The term "superheavy elements" was first coined for elements on a remote "island of stability" around atomic number 114 (Chap. 8). At that time this island of stability was believed to be surrounded by a "sea of instability". By now, as shown in Chap. 1, this sea has drained off and sandbanks and rocky footpaths, paved with cobblestones of shell-stabilized *deformed* nuclei, are connecting the region of shell-stabilized *spherical* nuclei around element 114 to our known world.

Perfectly acceptable, some authors are still using the term "superheavy element" in its traditional form; others have widened this region and have included lighter elements. It is generally agreed that the term "superheavy element" is a synonym for elements which exist solely due to their nuclear shell effects. From this point of view there are good arguments to begin the series of superheavy elements with element 104, rutherfordium. Because of the extra stability from nuclear shell-effects the known isotopes of rutherfordium exhibit half-lives of up to one minute. This is 16 orders of magnitude longer than the expected nuclear lifetime of 10^{-14} s these isotopes would survive without any extra shell stabilization. Taking 10^{-14} s as a realistic limit for a minimum lifetime of a system which can be called a chemical element, and assuming the absence of any shell effects, the world of chemical elements would be terminated at the end of the actinides. The appealing aspect of having the superheavy elements begin at element 104 is that this is identical with the beginning of the series of transactinide elements. The terms "superheavy elements" and "transactinide elements", in short "transactinides", are used with an equal meaning in this book.

One of the most important and most fascinating questions for a chemist is the one about the position of the superheavy elements in the Periodic Table of the Elements; how well accommodates the Periodic Table these elements as transition metals in the seventh period. Do the rules of the Periodic Table still hold for the heaviest elements? What is a valid architecture of the Periodic Table at its upper end? The main body of information to answer this question from our today's knowledge of the chemistry of superheavy or transactinide elements is embraced between the two mainly "nuclear" oriented chapters at the beginning and at the end.

One century after the beginning of most dramatic changes in physics and chemistry, after the advent of quantum theory and in the year of the 100th anniversary of Paul A.M. Dirac, modern relativistic atomic and molecular calculations clearly show the very strong influence of direct and indirect relativistic effects not only on electronic configurations but also on chemical properties of the heaviest elements. The actual state of the theoretical chemistry of the heaviest elements is comprehensively covered in Chap. 2. It does not only discuss most recent theoretical developments and results, where especially up to date molecular calculations dramatically increased our insights over the last decade, but it also relates these results to experimental observations.

The chemistry of superheavy elements always faces a one-atom-at-a-time situation—performing separations and characterizations of an element with single, short-lived atoms establishes one of the most extreme limits in chemistry. While large numbers of atoms and molecules are deeply inherent in the statistical approach to understanding chemical reactions as dynamic, reversible processes Chap. 3 discusses specific aspects how the behavior of single atoms mirrors properties of macro amounts.

A large variety of tools, from manual separation procedures to very sophisticated, automated computer-controlled apparatuses have been developed and are now at hand to study the chemical properties of these short-lived elements one-atom-at-a-time in the liquid phase and in the gas phase. It is demonstrated in Chap. 4 how this can be achieved, what kinds of set-ups are presently available and what the prospects are for future developments to further expand our knowledge.

The known chemical properties of superheavy elements are presented and discussed in Chaps. 5 and 7 based upon experimental results obtained from the liquid phase and from the gas phase, respectively. It is quite natural that there is a large body of information on group-4 element 104, rutherfordium, and group-5 element 105, dubnium, which are now under investigation for three decades. However, recent detailed studies demonstrate that these elements still hold many surprises. They sometimes exhibit rather unexpected properties. The chemistry of element 106, seaborgium, was first tackled in 1995 followed by a series of experiments in the aqueous and the gas phase. While most of them revealed a "surprisingly normal" behavior, at least one experiment indicated a deviation from an extrapolation in group 6. Even more challenging, because of the only very few numbers of atoms produced per day, were recent investigations on elements 107, bohrium, and 108, hassium, performed in one gas phase experiment each. This is presented in Chap. 7 together with an attempt to get a first glimpse of the chemical property of element 112. Will it chemically react like mercury or will it be much more inert; presumably due to strong influence of relativistic effects?

Empirical models are frequently applied in chemistry to relate experimental observations to physicochemical or thermodynamical quantities. This has extensively been used over several decades for the interpretation of experimental results obtained from gas phase adsorption processes and is still used to interpret the gas chromatographic results discussed in Chap. 7. These empirical procedures and correlations are outlined in Chap. 6 for a deeper understanding of one of the possible ways to interpret experimental findings from gas phase chemistry.

All the authors of the individual chapters are describing the up-to-date ongoing research in their field where they are leading experts and give a thorough and comprehensive review of our today's knowledge. The individual chapters were finished between mid of the year and November of the year 2002. Pictures of the people involved in many of the described experiments, photos of the instruments and more details on experiments and results can be found on the web-page http://www.gsi.de/kernchemie.

I wish to acknowledge the contributions of Jan Willem Wijnen and Emma Roberts from the Kluwer Academic Publishers who started (JWW) and finalized (ER) this project with me. Many thanks go to the authors of the individual chapters

who enthusiastically agreed to contribute to this book and who spent so much time and effort to collect, judge and write up extensive amounts of material. Only thanks to them was it possible to provide such a far-reaching coverage of the chemistry of superheavy elements. Last, but definitely not least, its a great pleasure to thank Brigitta Schausten very much for helping me and the authors with hundreds of smaller or larger details which came up during the preparation of this book, and especially for her work on some of the graphics and for preparing the final format.

Darmstadt, December 2002 Matthias Schädel http://www.springer.com/978-3-642-37465-4

The Chemistry of Superheavy Elements
Schädel, M.; Shaughnessy, D. (Eds.)
2014, XIII, 521 p. 217 illus., 48 illus. in color., Hardcover
ISBN: 978-3-642-37465-4