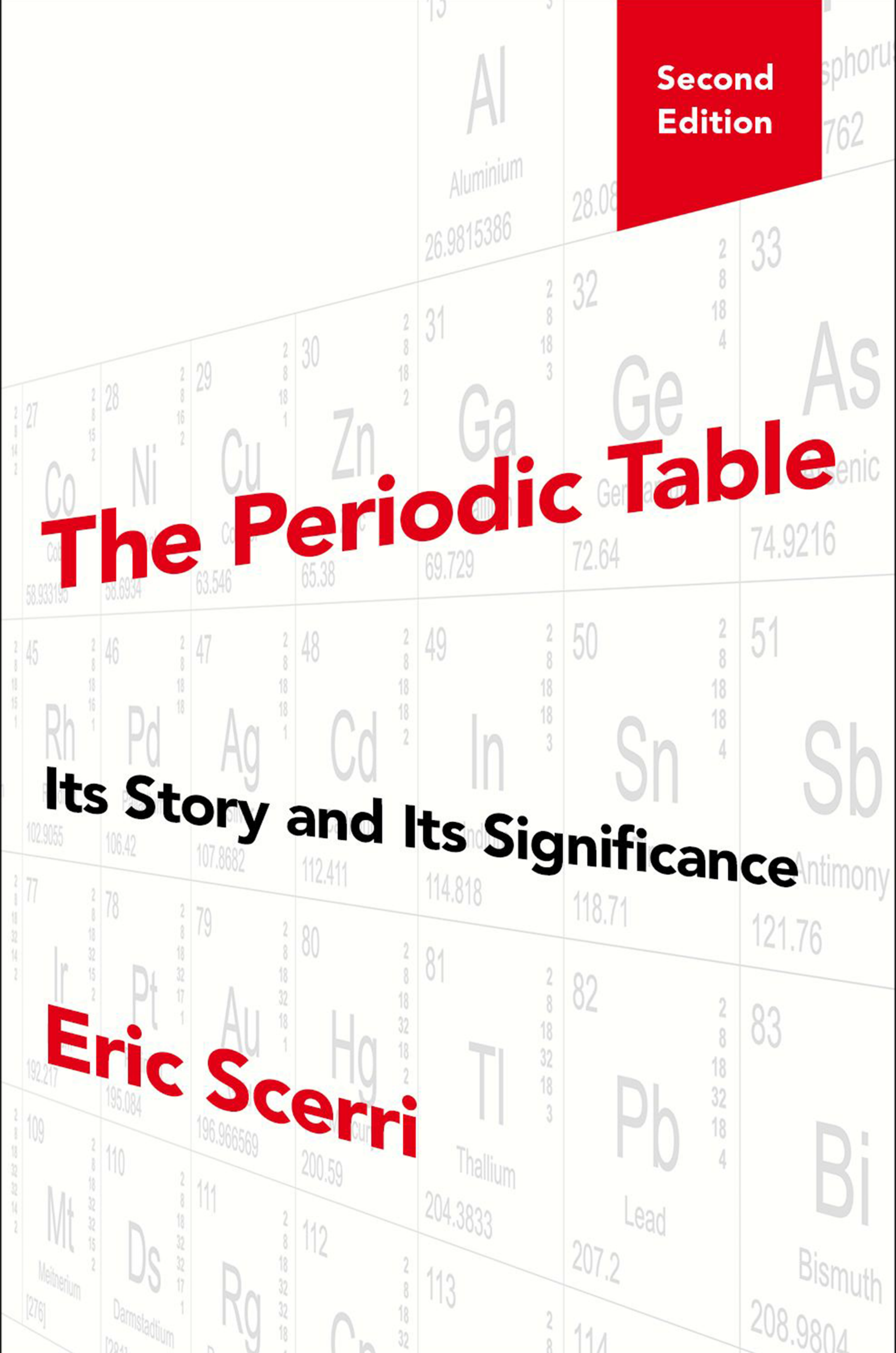

Second Edition

The Periodic Table

Its Story and Its Significance

Eric Scerri

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THE PERIODIC TABLE

Its Story and Its Significance

Second Edition

ERIC SCERRI

OXFORD
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Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
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Oxford University Press in the UK and certain other countries.

Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America.

First Edition published in 2006

Library of Congress Cataloging-in-Publication Data
Names: Scerri, Eric R., author.
Title: The periodic table : its story and its significance / Eric Scerri.
Description: 2nd edition. | New York, NY : Oxford University Press, [2019] |
Includes bibliographical references and index.
Identifiers: LCCN 2019008921 (print) | LCCN 2019017263 (ebook) |
ISBN 9780190914370 (updf) | ISBN 9780190914387 (epub) |
ISBN 9780190914363 (cloth : alk. paper)
Subjects: LCSH: Periodic table of the elements. | Chemical elements. |
Mendeleyev, Dmitry Ivanovich, 1834–1907. | Chemistry—History.
Classification: LCC QD467 (ebook) | LCC QD467 .S345 2019 (print) |
DDC 546/.8—dc23
LC record available at https://lccn.loc.gov/2019008921

1 3 5 7 9 8 6 4 2
Printed by Sheridan Books, Inc., United States of America

Dedication

I dedicate this book to my parents, Ines and Edward Scerri, for steering me toward the scholarly life. The book is also dedicated to my wife, Elisa Seidner, for her love and support and for helping to design the front cover.

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PREFACE TO THE SECOND EDITION

The publisher has requested that I update this book to coincide with 2019, the International Year of the Periodic Table (IYPT) that marks the 150th anniversary of Mendeleev's 1869 paper announcing the first fully mature periodic table. I have been anticipating a second edition for some time and have built up a large folder containing messages and letters from readers who have kindly pointed out typographical errors and various suggestions for improvements. I hope to have made as many of these improvements as possible, and, of course, I welcome any further suggestions to this ongoing project. My thanks to all those who have written to me during the 12-year period that has elapsed since the first edition appeared. Unfortunately, they are too numerous to name individually.

I have been very fortunate that the book has been generally well received and has been reviewed in more than 60 journals and magazines. These reviews have also served as guides to improvements. The book has been translated into several languages during which process it received close scrutiny from experts and translators, who also contributed to broadening my knowledge of many aspects of science and history of science that are discussed.

The new edition introduces four new chapters – two are completely new, some others have been reworked. First of all, chapter 10 of the earlier book consisted of a motley collection of topics, which some commentators rightly suggested should be separated. The material on "more chemistry" has now been removed to a separate chapter that serves to close the book. I think it helps to remember that, when all is said and done, the periodic table remains primarily in the domain of chemistry, although the relationship between chemistry and the underlying explanation from physics remains as the underlying theme of the book.

Similarly, the material on alternative forms of the periodic table that was in the original chapter 10 is now in another new chapter that is greatly expanded to review recent developments, such as the question of the placement of helium and the question of which elements belong to group 3 of the periodic table. These alternative forms of the periodic table continue to arouse interest from amateurs all the way to professional chemists, physicists, and philosophers of science and highlight the important point that the periodic table is by no means a *fait accompli*.

Chapter 9, on the quantum mechanical account of the periodic table, has now been greatly expanded to include some recent work on the perennial question of the occupation and ionization of the 4s and 3d orbitals as well as the question of anomalous configurations, such as those that occur in the atoms of chromium and copper.

Two completely new chapters have then been added. The first of these chapters is on what I call the seven missing infra-uranium elements, that is, the seven elements that remained to be discovered between hydrogen and uranium, following the discovery of the concept of atomic number. Another new chapter consists of an account of the synthetic elements that have been "discovered," including the very recently named quartet of elements that serve to complete the seventh row of the table and indeed to complete the entire periodic table for the first and probably the last time in the foreseeable future. Needless to say, this is a somewhat artificial feature since it depends on which representation of the periodic table one is referring to. On the left-step periodic table, which is attracting increasing attention from periodic table scholars, the table will only become complete after elements 119 and 120 are synthesized.

The book ends with a compilation of all the references that appear in each chapter that have been collected together in alphabetical order for the convenience of the reader, as well as what is hopefully the most complete listing of books on elements and the periodic table in several languages. Finally I have added a list of my own articles on the periodic table as well as related concepts.

Eric Scerri
Los Angeles, 2019
www.ericscerri.com

New Credits

Credits for all newly introduced figures have been added to the figures and are not listed together as they were in the first edition.

PREFACE TO THE FIRST EDITION

This book has been in the making for about six years, although perhaps I should say about twenty years since it was that long ago that I undertook my Ph.D. at what was then Chelsea College, University of London, under the excellent supervision of the late Heinz Post. Of course, I could go back even further and mention that my love affair with the periodic table began when I was still in my teens and attending Walpole grammar school in the West London borough of Ealing.

Now that this book is completed, I have the opportunity to thank all those who contributed to it either directly or indirectly as colleagues or mentors at various stages of my own development. At Walpole grammar school, Mrs. Davis was the chemistry teacher who noticed that I was fooling around at the back of the class and ordered me to sit in the front row. At this point, I had no choice but to listen to the lesson, and I soon discovered that chemistry was rather interesting.

Moving on to Westfield College, which was part of the University of London, I had many wonderful professors, among them John Throssell and Bernard Aylett, a theoretician and an inorganic chemist, respectively. This was followed by a year of theoretical work at Cambridge under the great David Buckingham, who despaired of my asking too many philosophical questions. Then I moved to Southampton University, where I obtained a Master of Philosophy degree in Physical Chemistry with the inimitable Pat Hendra. At this point, I began teaching chemistry in high schools and tutorial colleges. I eventually went back to research and wrote my Ph.D. in history and philosophy and philosophy of science on the question of the reduction of chemistry to quantum mechanics. I cannot overestimate the debt that I owe to Heinz Post, and as all who know him recall, he was perhaps the nearest thing to the archcritic Wolfgang Pauli that ever graced the philosophy of science scene in the United Kingdom. Not that I ever witnessed Pauli, however.

It was Heinz Post who encouraged me to try to develop the philosophy of chemistry, which I have sought to do ever since. I think it was also Heinz who first planted the idea of my going to the United States to teach and carry out research. But before moving on to my story in the United States, let me pause to mention a few other folks in London who have been influential and helpful: Mike Melrose, a theoretical chemist from King's College, London, and John Worrall from the London School of Economics. It has been a great privilege to have subsequently coauthored an article with each of them.[1]

I went to the United States as a postdoctoral fellow at Caltech. Here I must thank my colleagues Diana Kormos-Buchwald, Fiona Cowie, Alan Hayek, and James Woodward in the Humanities Division. I subsequently went for a year to Bradley University in the heart of Illinois, where I was warmly received by Don Glover and Kurt Field, among others, in the chemistry department. Then followed another visiting professorship at Purdue University, where I interacted mainly with George Bodner and historian–chemist–educator Derek Davenport. In the year 2000, I moved to the chemistry department at UCLA, where I am blessed with numerous great colleagues, among others, Miguel Garcia-Garibay, Robin Garrell, Steve Hardinger, Ken Houk, Herb Kaesz, Richard Kaner, Laurence Lavelle, Tom Mason, Craig Merlic, and Harold Martinson.

In addition, I am grateful to all the members of the International Philosophy of Chemistry Society, which a small group of us founded in the early 1990s after we realized that there were a sufficient number of people with an interest in this field.[2] My thanks to Michael Akeroyd, Davis Baird, Nalini Bhushan, Paul Boogard, Joseph Earley, Rom Harré, Robin Hendry, David Knight, Mark Leach, Paul Needham, Mary Jo Nye, Jeff Ramsay, Joachim Schummer, Jaap van Brakel, Krishna Vemulapalli, Stephen Weininger, Michael Weisberg, and many others.

Perhaps the largest group to acknowledge consists of the many scholars of the periodic table from diverse fields, who include Peter Atkins, Henry Bent, Bernadette Bensaude, Nathan Brooks, Fernando Dufour, John Emsley, Michael Gordin, Ray Hefferlin, Bill Jensen, Masanori Kaji, Maurice Kibler, Bruce King, Mike Laing, Dennis Rouvray, Oliver Sachs, Mark Winters, and others.

I thank my various coeditors at Foundations of Chemistry, both past and present, including John Bloor, Carmen Giunta, Jeffrey Kovac, and Lee McIntyre. I thank my UCLA colleagues in the Department of Philosophy, including Calvin Normore, Sheldon Smith, and Chris Smeenk, and in the Department of History, Ted Porter and Norton Wise.

My thanks to members of various online discussion lists, including Chemed, History of Chemistry, Philchem, Hopos, and CCL (Computational Chemistry Listserver), with whom various points were ironed out, sometimes amidst heated debate.

Last but not least, there are a number of people who helped me specifically with the compilation of this book, especially with collecting photos and images. They include Ted Benfey, Gordon Woods, Ernst Homberg, Frenando Dufour, and Susan Zoske; George Helfand and Andreana Adler from the photographic unit at UCLA who scanned the diagrams; and Marion Peters in the chemistry department library. Special thanks to Daniel Contreras, who was always patient in helping me to unearth those obscure early sources. I am sure he grew quite tired of ordering volumes of *Science News* for me from the vaults on the other side of campus. Special thanks also go out to Goeffrey Rayner Canham and William Brock for their detailed comments on the entire manuscript and to Jan Van

Spronsen, the doyen of the periodic table, for his comments on some early chapters of the book.

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Gordon Woods for providing the photo and permission for "The Consolidators of the Periodic Law."

Fernando Dufour for providing the photo of his own 3-D periodic system.

Article Credits

I have drawn from my own previous articles and particularly from four publications:

British Journal for the Philosophy of Science, 42, 309–325, 1991 (published by Oxford University Press, UK).

Annals of Science, 51, 137–150, 1994 (published by Taylor & Francis)

Studies in History and Philosophy of Science, 32, 47–452, 2001 (published by Elsevier)

Foundations of Chemistry, 6, 93–116, 2004 (published by Springer)

All these articles were used by permission from the publishers.

Notes

1. M.P. Melrose, E.R. Scerri, Why the 4s Orbital Is Occupied before the 3d, *Journal of Chemical Education*, 73, 498–503, 1996; E.R. Scerri, J. Worrall, Prediction and the Periodic Table, *Studies in the History and Philosophy of Science*, 32, 407–452, 2001.

2. At about the same time, the official journal of the society, *Foundations of Chemistry,* was also started.

INTRODUCTION

> As long as chemistry is studied there will be a periodic table. And even if someday we communicate with another part of the universe, we can be sure that one thing that both cultures will have in common is an ordered system of the elements that will be instantly recognizable by both intelligent life forms.
>
> J. Emsley, *The Elements*

The periodic table of the elements is one of the most powerful icons in science: a single document that captures the essence of chemistry in an elegant pattern. Indeed, nothing quite like it exists in biology or physics, or any other branch of science, for that matter. One sees periodic tables everywhere: in industrial labs, workshops, academic labs, and of course, lecture halls.

The Periodic System of the Elements

It is sometimes said that chemistry has no deep ideas, unlike physics, which can boast quantum mechanics and relativity, and biology, which has produced the theory of evolution. This view is mistaken, however, since there are in fact two big ideas in chemistry. They are chemical periodicity and chemical bonding, and they are deeply interconnected.

The observation that certain elements prefer to combine with specific kinds of elements prompted early chemists to classify the elements in tables of chemical affinity. Later these tables would lead, somewhat indirectly, to the discovery of the periodic system, perhaps the biggest idea in the whole of chemistry. Indeed, periodic tables arose partly through the attempts by Dmitri Mendeleev and numerous others to make sense of the way in which particular elements enter into chemical bonding.

The periodic table of the elements is a wonderful mnemonic and a tool that serves to organize the whole of chemistry. All of the various periodic tables that have been produced are attempts to depict the periodic system. The periodic system is so fundamental and all pervasive in the study of chemistry, as well as in professional research, that it is often taken for granted, as very familiar things in life so frequently are.

In spite of the central, or some might say homely, role of the periodic table, few authors have felt drawn to write books on its evolution. There is no book that deals adequately with the historical, and especially the conceptual, aspects of the periodic system or its significance in chemistry and science generally.[1] It is with the aim of injecting a more philosophical treatment to understanding the periodic system that the present work has been undertaken. I make no apologies for this approach, which I believe is long overdue and can perhaps be understood in the context of the almost complete neglect of the study of the philosophy of chemistry until its recent resurgence in the mid-1990s.

Only two major books on the periodic system have appeared in the English language, one of these being a translation from the Dutch original.[2] The more contemporary of these books, published in 1969 and authored by Johannes van Spronsen, is an excellent and detailed exposition of the history of the periodic system. One of the few omissions from van Spronsen's book is a discussion of the way in which modern physics is generally claimed to have explained the periodic system. Van Spronsen at times accepts the usual unspoken, or sometimes explicit, claim that the periodic system has been "reduced" to quantum mechanics, to use a phrase popular in philosophy of science.[3] In my own view, the extent to which quantum mechanics reduces the periodic system is frequently overemphasized. Of course, quantum mechanics provides a better explanation than was available from the classical theories of physics, but in some crucial respects the modern explanation is still lacking, as I hope to explain.

The only other serious treatise on the periodic system, written in English, is a masterly and detailed exposition, published in 1896, by F.P. Venable of the University of North Carolina–Chapel Hill.[4] It goes without saying that, for all its strengths, this book is severely limited, as it covers a period that ended more than 100 years ago, before modern physics began to exercise a major influence on the way the periodic system is understood.

There is also a compilation of more than 700 representations of the periodic system in a book by E. Mazurs, who devoted a lifetime of study to the topic. However, this book is neither a history nor a philosophy of the periodic system but a rather idiosyncratic attempt to develop a system of classification for periodic classifications themselves. It serves as a repository of the huge variety of forms in which the periodic system has been represented, and it is a testament to how expansive and energetic the quest for the ultimate form of the periodic system has been.[5] This quest appears to be with us to this day, an issue that will be taken up in later chapters. Another virtue of the Mazurs book is that it provides a wealth of references to the primary and secondary literature on the periodic system, although this, too, is now some 35 or so years out of date.[6] The textbook author Peter Atkins has published a short popular book on the periodic system.[7] There are also a number of books, including those by Puddephatt and Monaghan,[8] as well as by Cooper,[9] Pode,[10] and Sanderson,[11] which use the periodic system as a means of presenting the chemistry of the elements but make little attempt to evaluate critically the foundational basis of the system. The continuing interest in the periodic system is further exemplified by the appearance of books aimed at the nonspecialist by Strathern, Sacks, Morris, Kean, Aldersey-Williams, and Gray.[12] Although the focus of these books is on chemistry generally, they contain sections on the development of the periodic system. Recently, M. Gordin has published a biography of Mendeleev, which is historically sensitive as well as scientifically accurate, and benefits from the author's first-hand knowledge of the original Russian documents.[13] In addition W.B. Jensen has published a translation of many of Mendeleev's key articles.[2]

The Elements

In this book I examine the concept of an element in some detail, starting from the views expressed by the ancient Greek philosophers and bringing us right up to modern times. Although this topic has seldom been discussed in the context of the evolution of the periodic system, it is difficult to fully understand the classification of the elements without first attempting to understand what an element is and how such a concept has changed over time. There is a sense in which ancient views on the nature of the elements have not been entirely rejected, although they have been changed considerably.

The study of the nature of elements and compounds is at the heart of much of Aristotle's philosophy of substance and matter and even his most general views of "being" and "becoming." This was also true of many of the pre-Socratic philosophers, who were the first to discuss and theorize about the elements. About 20 centuries later, the nature of the elements was a major issue in the revolution of chemistry. Antoine Lavoisier seems to have been one of the first chemists to renounce the metaphysical view of the elements, which he replaced with a form of empiricism, which considered only substances that could actually be isolated as elements. Elements in this latter sense of the term are often called "simple substances."[14]

This essentially philosophical question regarding the nature of elements returned and profoundly shaped the views of Mendeleev, who is arguably the leading discoverer of the periodic system. Indeed, it appears that Mendeleev may have been able to make more progress than some of his contemporaries, who were also developing periodic systems, because of his philosophical ideas about the nature of the elements. Even in the twentieth century, following the discovery of isotopes, fierce debates were waged on the nature and correct definition of the term "element."[15]

Mendeleev held a dual view on the nature of elements, whereby they could be regarded as unobservable basic substances and also as Lavoisier's simple substances at the same time. Mendeleev thus acknowledged one of the central mysteries running throughout the long history of chemistry, which is the question of how, if at all, the elements survive in the compounds they form when they are combined together. For example, how can it be claimed that a poisonous gray metal like sodium is still present when it combines with a green poisonous gas chlorine, given that the compound formed, sodium chloride, or common table salt, is white and not only nonpoisonous but also essential for life? These are the kinds of questions the ancient Greek philosophers wrestled with while trying to understand the nature of matter and change. As I will show, such questions are still with us today, although some aspects of them have been explained by modern physical theory and the theories of chemical bonding.

Alchemy

Although in this book I briefly examine the nature of the elements, and of atomism from their earliest origins, not too much time is devoted to issues surrounding alchemy, for various reasons. First, the study of alchemy has been fraught with the obvious difficulties of trying to understand a complex set of practices spanning a number of areas, including what today would be considered religion, psychology, numerology, metallurgy, and so on. In addition, alchemical texts were frequently shrouded in deliberate mystery and obfuscation to protect the practitioners, who were regularly accused of being charlatans. Such mystery also served to restrict alchemical knowledge to a few initiates belonging to particular secret cults.

The question of whether modern chemistry is a direct outgrowth of alchemy, or whether alchemy's fundamental tenets had to be rejected in order for chemistry to get started, has been the source of much debate and continues to be disputed by scholars. All I do here is refer the reader to a few detailed treatments containing more serious discussion of this vast field of study.

One interesting aspect of this issue that has emerged in recent years is a questioning of the notion that the giants of modern science, such as Isaac Newton and Robert Boyle, turned their backs on alchemy. Starting about 40 years ago, historians of science, and Betty Jo Dobbs in particular, have argued rather persuasively that Newton was a dedicated alchemist and that he might even have devoted more time to this field than to his work in theoretical physics, for which he is now universally revered. More recently, Lawrence Principe has re-alchemized Boyle in a similar way that Dobbs had re-alchemized Newton.[16] Through painstaking analysis of Boyle's writing, Principe argues that, contrary to the accepted view, Boyle did not reject alchemical ways in his seminal book, *The Sceptical Chymist*. Indeed, Principe writes:

> We now see that Boyle himself in no way rejected transmutational alchemy but rather pursued it avidly and appropriated several of its theoretical principles....Boyle was not as "modern" as we thought, nor alchemy as "ancient." What we are witnessing, then, is a rapprochement between what have been previously seen as two separate and irreconcilable halves of the history of chemistry.[17]

A Philosophical Approach

As I have already suggested, the study of the periodic system is philosophically important in several ways. Let me be a little more specific. For some time now, philosophers of science have realized that they have placed too much emphasis on the study of scientific theories and not enough on other important aspects of science, such as experimental work and scientific practice in general.[18] This has led many researchers to initiate the study of the philosophy of experimentation. But even within the philosophical investigation of theoretical work, there has been a growing sense that there is much more to scientific theorizing than just appealing to high-level theories.

In many cases, the theory in question is too difficult to apply, and so scientists tend to base their work on models and approximations. The full acceptance of this fact has produced a subdiscipline that studies the nature of scientific models.[19] And yet, as I argue in this book, the periodic table of chemistry is neither a theory nor a model but more akin to an "organizing principle," for want of a better term.[20] This book is partly an attempt to encourage philosophers of science to study the periodic table as an example of yet another scientific entity that does a lot of useful scientific work without being a theory.[21]

Another reason why the periodic table is philosophically important is that it provides an excellent testing ground for the question of whether chemistry is nothing but physics deep down or, as philosophers like to say, whether chemistry reduces to physics. But even asking such a question has become controversial in modern scholarship. The view that physics is the most fundamental of the sciences or, indeed, the very notion of one field being more fundamental than another one is under severe threat from disciplines such a literary criticism, cultural anthropology, and postmodern critiques of science.[22] Such issues have become highly controversial in recent times, producing what is perhaps the major debate in today's academic world, namely, the "science wars." Many scholars, scientists, and intellectuals find themselves pitted against each other over the question of whether science provides a form of objective truth or whether it is no more than a social construction not necessarily governed by the way the world actually is. The traditional view of scientific objectivity is increasingly regarded as a thing of the past, and some scholars are even prepared to embrace a form of relativism, or the view that all forms of knowledge are equally valid.[23]

But many others believe the question of fundamentalism and reduction can still be studied within the context of science. One can still consider the more modest question of whether chemistry reduces to its sister science of physics. This question can be approached in a scientific manner by examining the extent to which chemical models or, indeed, the periodic system, can be explained by the most basic theory of physics, namely, quantum mechanics. It is this question that forms the underlying theme for this entire book, and it is a question that is addressed more and more explicitly in later chapters as the story reaches the impact of modern physical theories on our understanding of the periodic system.

The Evolution of the Periodic System

As I try to show in this book, several intermediate and anticipatory steps preceded every important stage in the development of the periodic system. Of all the major developments in the history of science, there may be no better example than that of the periodic system to argue against Thomas Kuhn's thesis that scientific progress occurs through a series of sharp revolutionary stages.[24] Indeed, Kuhn's insistence on the centrality of revolutions in the development of science and his efforts to single out revolutionary contributors has probably unwittingly contributed to the retention of a Whiggish history of science, whereby only the heroes count while blind alleys and failed attempts are written out of the story.[25]

Science is, above all, a collective endeavor involving a large variety of people working sometimes in teams, sometimes in isolation, sometimes aware of the work of their contemporaries and sometimes not.[26] When trying to examine the development of a system of knowledge such as the periodic system, it may be more important to look at the overall picture complete with wrinkles than to concentrate on who came first or whether a certain development really is an anticipation of a later one. Nevertheless, since priority issues are part of this fascinating story, in this book I try to give an account of some of the most important ones without claiming to provide the final word on any of the long-standing disputes.

Perhaps a further word on a different sense of the term "Whiggism" is appropriate. Since this book is not intended as a work of historical scholarship, there will be many instances in which the story will be driven by what eventually took place in the history of science. I make no apology for this approach since part of the interest is in trying to trace the development of the modern periodic system. For example, when discussing triads of elements, which were based on atomic weights, I will not avoid looking ahead to the use of atomic numbers to see what effects this change might have on the validity or otherwise of triads.

So without further delay, what follows is a brief synopsis of the chapters of the present book. I adopt a historical approach in order to convey the gradual evolution that has taken place around the chemical icon that is the periodic system. However, my primary concern is the evolution of concepts and ideas rather than trying to produce a work of detailed historical scholarship.[27] At times, I even use strictly ahistorical examples to illustrate particular points.

The book takes the reader on an interdisciplinary tour of the many areas of science that are connected with the periodic system, including physics, mathematics, computational methods, history and philosophy of science, and of course, chemistry. The story begins with the pre-Socratic philosophers in ancient Greece and progresses through the birth of atomism and on to Aristotle's four elements of earth, water, fire, and air. By the Middle Ages, when the full impact of alchemy was reached, a few other elements, such as sulfur and mercury, were added to the list. But this book does not explore the state of chemical knowledge of the elements in the Middle Ages, early medicine, or Arabic chemistry, although these are important preliminaries to modern chemistry. Nor does it visit the theory of phlogiston, which was deposed by the chemical revolution; it merely examines Lavoisier's famous list of 37 fundamental substances.[28]

Instead, the story of the periodic system will take the plunge with the work of William Prout, Johann Döbereiner, Leopold Gmelin, and others who began to explore numerical relationships among the elements in addition to the previously known chemical analogies between them. We encounter the first true periodic system, which was the helical periodic system of Alexandre De Chancourtois, as well as the early periodic systems of William Odling, Gustavus Hinrichs, Jean-Baptiste André Dumas, Max Pettenkofer, John Newlands, and Julius Lothar Meyer, culminating with Mendeleev's tables and his deductions concerning existing as well as completely new elements. In each case, we look into some of the historical background involved as well as specific aspects of the periodic system proposed.

The discovery in the 1890s of the noble gases, a group of elements that did not initially appear to fit into the periodic system, is analyzed, as is the eventual resolution of this problem. The turn of the twentieth century saw the discovery of radioactivity, which led to new ideas about the structure of the atom from J.J. Thomson and Ernest Rutherford. Very soon, isotopes of many of the elements were discovered, and this produced a major challenge to the periodic system. Niels Bohr, Wolfgang Pauli, Erwin Schrödinger, and Werner Heisenberg, who provided the modern explanation of the periodic system in terms of orbiting electrons and quantum numbers, continued the invasion of physics into the understanding of the periodic table.

Whenever scientists are presented with a useful pattern or system of classification, it is only a matter of time before they begin to ask whether there may be some underlying explanation for the pattern. The periodic system is no exception. Attempts to produce explanations of the periodic system have led to major advances in areas of science other than chemistry, especially theoretical physics. The notion that the atom consists of a nucleus with electrons in orbit around it, which is taken for granted in modern science, originated when British physicist J.J. Thomson tried to explain the order of the elements displayed in the periodic table. Similarly, when Bohr, one of the founders of quantum mechanics, applied new ideas about the quantum of energy to the atom, he was specifically trying to obtain a deeper understanding of the periodic system of the elements.[29]

A few years later, Pauli produced his celebrated Exclusion Principle, which is now known to govern the behavior of all matter from materials used to make transistors to the matter in neutron stars. Pauli's original research, carried out in atomic physics, was initially an attempt to explain the form of the periodic system and why the various electron shells of the atom can contain only specific numbers of electrons. In the process, Pauli produced one of the most general principles known to science. His Exclusion Principle tells us, in simple terms, that an electronic orbital can contain only two electrons, which must have antiparallel spins.[30] A careful analysis of this principle and other general principles of quantum mechanics has produced a new discipline of quantum chemistry, which nowadays is exploited in the development of new materials from superconductors to pharmaceutical drugs.

Now a word on the subject of chemical education. Two of the leading discoverers of the periodic system, Lothar Meyer and Mendeleev, were outstanding chemical educators who developed their versions of the periodic system while writing chemistry textbooks. One of the principal roles of the periodic table is as a teaching tool, given that it unifies so much chemical information and establishes unity amidst the diversity of chemical phenomena. In recent years, there has been a growing awareness that chemistry is being taught as though it were a subdiscipline of physics. This tendency has occurred because physics, in the form of quantum mechanics, has been successful in explaining many aspects of chemistry. But this success is frequently overemphasized.

Chemistry students are increasingly fed a diet of orbitals, electronic configurations, and other theoretical concepts instead of being exposed to the more tangible colors, smells, and even explosions of "real chemistry." Some authors advocate making chemical education more "chemical," while at the same time introducing students to the necessary concepts in modern physics. In such an endeavor, the periodic table can serve as an excellent link between macroscopic chemical properties and the underlying quantum mechanical explanations.

But in addition to any pedagogical implications, the relationship between chemistry and physics has become increasingly important in the philosophy of science. In particular, the recent growth of the philosophy of chemistry as a distinct subdiscipline has been based to some extent on examining the question of the reduction of chemical laws, chemical models, and representations, such as the periodic system, to fundamental physics.[31]

But even before the advent of the philosophy of chemistry, the question of the reduction of scientific theories to successor theories has been an important concern, as has the question of whether any of the special sciences reduce to basic physics. Broadly speaking, as the logical positivist approach to philosophy has been superseded, claims for the reduction of theories and fields of science have been increasingly challenged.[32] The failure to establish the full reduction of theories and the special sciences has been one reason for the demise of logical positivism in philosophy. But this failure of reduction in the manner prescribed by logical positivism has not led to the abandonment of another central tenet of logical positivism, namely, a belief in the unity of the sciences.[33]

In contemporary philosophy of science, the question of reduction is no longer approached in an axiomatic manner. It is rather pursued in a more naturalistic manner by examining the extent to which the periodic system, for example, can be deduced from the first principles of quantum mechanics. While this approach is still rigorous, it is not rigorous in the sense of using formal logic to establish the required connection.[34] It is rather by examining the extent to which the facts in the secondary science, if one must use such terms, can be deduced in an *ab initio* manner, to use a contemporary phrase, from computational chemistry. One needs to examine the way in which the Schrödinger Equation explains the structure of the periodic system, a topic that is specifically addressed in chapter 9. But leading up to these more contemporary developments, there were already claims made by Bohr, and on his behalf, that he had given a reduction of the periodic system using just the old quantum theory.[35] The story of the periodic system is inextricably linked with the increasing influence of modern physics upon chemistry. The question of reduction in many forms thus underlies the developments discussed in this book.

And even further back in the story of the periodic system, one can see the influence of numerical approaches dating back to Prout's hypothesis and Döbereiner's triads, both of which predate the discovery of the periodic system. Hence, it is not just chemistry that enables one to classify the elements but a combination of chemistry with the urge to reduce, in the most general Pythagorean sense of describing facts mathematically. The story of the periodic system is the story of the blending of chemistry, Pythagoreanism, and, most recently, quantum physics.

If one takes a realistic view concerning the periodic law, one might claim that there is a definite fact of the matter concerning the point at which approximate repetition occurs among the elements as the atomic number sequence increases. For example, the position of the element helium has led to a certain amount of debate. While most chemists insist that the element is a noble gas, an appeal to the electronic configuration of its atoms suggests that it might be placed among the alkaline earths. A chemist having an antirealist disposition on these issues might consider that the representation of the elements is a matter of convention and that there is no real fact of the matter concerning where helium and other troublesome elements should be placed. These issues will be discussed in chapter 10, which also considers the astrophysical origin of the elements as well as some unusual chemical regularities embodied in the periodic table.

The question of reduction raises another interesting issue concerning the reduction of chemistry to quantum mechanics. It appears that most chemists are quite willing to accept the reductive claims from physics insofar as it bestows greater theoretical underpinning upon chemistry. Nevertheless, in cases such as the positioning of helium, chemists retain the right to classify the element in chemical terms even at the risk of overruling the findings of the reducing science.

Along with the realist view of the periodic system, as referred to above, comes the question of whether to regard the elements as "natural kinds," meaning realistic scientific entities that are differentiated by nature itself rather than by our human attempts at classification.[36] This in turn opens up further dialogue with mainstream philosophy of science, which concerns itself with the question of natural kinds. In philosophy of biology, species have been deemed not to be natural kinds since biological species evolve over time. Many philosophers have sought to locate natural kinds at the chemical level.[37] Elements, in particular, are regarded by many as the quintessential natural kind term. To be gold is to possess atomic number 79 and vice versa. Natural kinds have been regularly invoked in the debates among philosophers of language concerning how linguistic terms such as "gold" or "water" refer to objects in the world. According to the influential Kripke-Putnam view, we are urged to take a scientific view of natural kind terms. The term "water," for example, is to be taken as denoting just what modern science stipulates water to be, which is usually taken to be molecules of H_2O. This approach raises many issues that continue to exercise contemporary philosophers of science. Water is not simply H_2O since it may contain impurities or may be present in ionized form, to cite just two of many objections that have been raised.[38] Even the notion that elements may be natural kinds has been criticized on the basis of the existence of isotopes of many elements. Not all atoms of gold have the same mass, and so it has been claimed that gold is not a unique natural kind.[39]

It appears that one of the best ways to explore the relationship between chemistry and modern physics is to consider the status of the periodic system.[40] Given the renewed interest in the philosophy of chemistry and in the periodic system itself,[41] a reassessment of these basic issues is now required, and this is attempted in the chapters of this book.

Notes

1. There have only been three conferences specifically on the periodic table. The first was held in 1969 as part of the celebrations commemorating the centenary of Mendeleev's famous table of 1869 [M. Verde (ed.), *Atti del Convegno Mendeleeviano*, Accademia delle Scienze di Torino, 1971]. The second was held as recently as 2003 in Banff, Canada [D. Rouvray, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Science Studies Press, Bristol, UK, 2004]. The third such conference took place in Cusco, Peru, in 2004 [E. Scerri, G. Restrepo, *Mendeleev to Oganesson*, Oxford University Press, New York, 2018]. Appropriately enough, the fourth international meeting will take place in 2019, the International Year of the Periodic Table, to celebrate the 150th anniversary of the publication of Mendeleev's table and will be in St. Petersburg, Russia.

2. I am referring to scholarly books on the periodic table. In addition, for a translation of Mendeleev's main journal articles, see W.B. Jensen, *Mendeleev on the Periodic Law, Selected Writings, 1869–1905*, Dover Publications, Mineola, NY, 2005.

3. J. van Spronsen, *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969. I find it embarrassing to make this criticism given the enormous debt I owe to van Spronsen's wonderful book on the periodic system.

4. F.P. Venable, *The Development of the Periodic Law*, Chemical Publishing Co., Easton, PA, 1896.

5. E. Mazurs, *The Graphic Representation of the Periodic System During 100 Years*, University of Alabama Press, Tuscaloosa, 1974. In addition, Mazurs has given some arguments for the adoption of a symmetrical representation of the periodic system.

6. For a now somewhat dated bibliography of secondary articles on the periodic system, which emphasizes philosophical works, see E.R. Scerri, J. Edwards, Bibliography of Literature on the Periodic System, *Foundations of Chemistry*, 3, 183–196, 2001. A revised bibliography will appear soon in the same journal.

7. P.W. Atkins, *The Periodic Kingdom*, Basic Books, New York, 1995. Also see E.R. Scerri, A Critique of Atkins' Periodic Kingdom and Some Writings on Electronic Structure, *Foundations of Chemistry*, 1, 287–296, 1999.

8. R.J. Puddephatt, P.K. Monaghan, *The Periodic Table of the Elements*, Oxford University Press, Oxford, 1985.

9. D.G. Cooper, *The Periodic Table*, Plenum Press, New York, 1968.

10. J.S.F. Pode, *The Periodic Table: Experiment and Theory*, Wiley, New York, 1973.

11. R.T. Sanderson, *The Periodic Table of the Chemical Elements*, School Technical Publishers, Ann Arbor, MI, 1971.

12. P. Strathern, *Mendeleyev's Dream*, Thomas Dunne Books, New York, 2001; O. Sacks, *Uncle Tungsten*, Alfred Knopf, New York, 2001; R. Morris, *The Last Sorcerers: Atoms, Quarks and the Periodic Table*, Walker & Co., New York, 2003; S. Kean, *The Disappearing Spoon*, Little, Brown, New York, 2010; H. Aldersey-Williams, *Periodic Tales*, Penguin Viking, London, 2011; T. Gray, *The Elements*, Black Dog and Leventhal, New York, 2009.

13. M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004. A revised edition was published in 2019 by Princeton University Press under the same title.

14. Lavoisier did not fully renounce the idea of elements as principles, however. For example, he regarded heat light and oxygen as examples of such principles.

15. A collection of articles edited by Elena Ghibaudi and myself on the concept of "element" is currently in preparation and will be published by Oxford University Press.

16. B.J.T. Dobbs, M.C. Jacob, *Newton and the Culture of Newtonianism*, Humanity Books, Amherst, NY, 1998.

17. Lawrence Principe, *The Aspiring Adept: Robert Boyle and His Alchemical Quest: Including Boyle's "Lost" Dialogue on the Transmutation of Metals*, Princeton University Press, Princeton, NJ, 1998, quoted from p. 220.

18. A number of detailed studies on philosophical aspects of scientific experiments now exist, including David Gooding, Trevor Pinch, Simon Schaffer, *The Uses of Experiment: Studies in the Natural Sciences*, Cambridge University Press, New York, 1989; and Allan Franklin, *The Neglect of Experiment*, New York, Cambridge University Press, 1986.

19. E.g., the book on scientific models by the philosopher Nancy Cartwright, *How the Laws of Physics Lie*, Oxford University Press, Oxford, 1983.

20. My disagreement with authors who believe the periodic table to be a theory is expressed in E.R. Scerri, A Critique of Weisberg's "Who Is a Modeler?" *Foundations of Chemistry*, 14, 275–284, 2012.

21. D. Shapere, Scientific Theories and Their Domains, in F. Suppe (ed.), *The Structure of Scientific Theories*, Illinois University Press, Urbana, 518–599.

22. The literature in this area has grown tremendously in recent years. For discussions, see P.R. Gross, N. Levitt, *Higher Superstition*, Johns Hopkins University Press, Baltimore, MD, 1994; A. Sokal, Transgressing the Boundaries: Towards a Transformative Hermaneutics of Quantum Gravity, *Social Text*, 46–47, 217–252, 1996; J.A. Labinger, H. Collins, *The One Culture*? University of Chicago Press, Chicago, 2001.

23. G. Bodner, M. Klobuchar, D. Geelan, The Many Forms of Constructivism, *Journal of Chemical Education*, 78, 1107–1134, 2001. For a critical appraisal, see E.R. Scerri, Philosophical Confusion in Chemical Education Research, *Journal of Chemical Education*, 80, 468–474, 2003.

24. This is not to imply that Kuhn himself or anyone else I am aware of has argued that the development of the periodic system *did* represent a scientific revolution. On a related point, in a recent book I have argued that there are very few, if any, Kuhnian revolutions in science in general, and I have proposed an evolutionary account of the development of science. Eric Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016.

25. Related claims about Kuhn's conservatism are made in Steve Fuller, *Thomas Kuhn: A Philosophical History for Our Times*, University of Chicago Press, Chicago, 2000; and Mara Beller, *Quantum Dialogue: The Making of a Revolution*, University of Chicago Press, Chicago, 1999.

26. I have written a book that addresses this question and that criticizes Kuhn's view of revolutions in science. The study is based on the work of seven little-known scientists and amateurs who made significant contributions to early-twentieth-century chemistry and atomic physics. E. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016.

27. Readers interested in scholarly research on Mendeleev in particular should consult the work of a number of excellent contemporary historians of science, including N. Brookes, Developing the Periodic Law: Mendeleev's Work during 1869–1871, *Foundations of Chemistry*, 4, 127–147, 2002; M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004; and M. Kaji, Mendeleev's Discovery of the Periodic Table, *Foundations of Chemistry*, 5, 189–214, 2003.

28. Over the past 30–40 years, there has been a great deal of debate among historians of chemistry regarding Lavoisier's role in the chemical revolution and whether this was indeed a revolution or just the culmination of previous work begun by the likes of Georg Stahl. See articles by Gough, Siegfried, Perrin, and Holmes in A. Donovan (ed.), Chemical Revolution: Essays in Reinterpretation, *Osiris*, 2nd series, vol. 4, 1988.

29. The popular story found in most books is that Bohr was primarily concerned with explaining the spectrum of the hydrogen atom. But as Kuhn and Heilbron have convincingly argued, Bohr was not even aware of the problems with atomic spectra when he began applying quantum theory to the structure of the atom. T.S. Kuhn, J. Heilbron, The Genesis of the Bohr Atom, *Historical Studies in the Physical Sciences*, 3, 160–184, 1969.

30. Nevertheless, elementary particles do not literally spin in the way that the earth or a mechanical top does. A better description would be a classically nondescribable duplicity in the intrinsic angular momentum of electrons, which is indeed how Pauli first described what later became known simply as "spin."

31. My more recent thinking on this subject can be found in E. Scerri, The Changing Views of a Philosopher of Chemistry on the Question of Reduction, in E.R. Scerri, G. Fisher (eds.), *Essays in the Philosophy of Chemistry*, Oxford University Press, New York, 2016.

32. J.D. Trout, in R. Boyd, P. Gaspar, J.D. Trout (eds.), Reduction and the Unity of Science, *The Philosophy of Science*, MIT Press, Cambridge, MA, 1992, 387–392.

33. A few modern commentators appear to disagree in this respect and regularly advertise their support for the "disunity of science": J. Dupré, *The Disorder of Things, Metaphysical Foundations of the Disunity of Science*, Harvard University Press, Cambridge, MA, 1993; N. Cartwright, *How the Laws of Physics Lie*, Clarendon Press, Oxford, 1983; N. Cartwright, *Nature's Capacities and Their Measurement*, Oxford University Press, Oxford,

1989; P. Galison, D. Stump, *The Disunity of Science*, Stanford University Press, Palo Alto, CA, 1996.

34. For a more detailed treatment of this modern approach to the reduction of chemistry, see E.R. Scerri, Popper's Naturalized Approach to the Reduction of Chemistry, *International Studies in Philosophy of Science*, 12, 33–44, 1998.

35. K.R. Popper, Scientific Reduction and the Essential Incompleteness of All Science, in F.L. Ayala, T. Dobzhansky (eds.), *Studies in the Philosophy of Biology*, Berkeley University Press, Berkeley, CA, 1974, 259–284.

36. Zdenka Brzovic, Natural Kinds, *The Internet Encyclopedia of Philosophy*, ISSN 2161–0002, 2018. http://www.iep.utm.edu/nat-kind.

37. J. LaPorte, Chemical Kind Terms, Reference and the Discovery of Essence, *Noûs*, 30, 112–132, 1996; J. LaPorte, *Natural Kinds and Conceptual Change*, Cambridge University Press, New York, 2004.

38. J. van Brakel, *Philosophy of Chemistry*, Leuven University Press, Leuven, Belgium, 2000.

39. I believe that this criticism can be countered by appeal to the elements as basic substances in the sense used by Mendeleev. E.R. Scerri, Some Aspects of the Metaphysics of Chemistry and the Nature of the Elements, *Hyle*, 11, 2, 2005.

40. P. Bernal, Foundations of Chemistry: Special Issue on the Periodic System, *Journal of Chemical Education*, 79, 1420, 2002.

41. E.g., see an editorial in *Foundations of Chemistry* for the special issue on the periodic system, vol. 3, 97–104, 2001.

The Periodic Table

CHAPTER 1

THE PERIODIC SYSTEM

The Elements

In ancient Greek times, philosophers recognized just four elements—earth, water, air, and fire—all of which survive in the astrological classification of the 12 signs of the zodiac. At least some of these philosophers believed that these different elements consisted of microscopic components with differing shapes and that this explained the various properties of the elements. These shapes or structures were believed to be in the form of Platonic solids (figure 1.1) made up entirely of the same two-dimensional shape. The Greeks believed that earth consisted of microscopic cubic particles, which explained why it was difficult to move earth. Meanwhile, the liquidity of water was explained by an appeal to the smoother shape possessed by the icosahedron, while fire was said to be painful to the touch because it consisted of the sharp particles in the form of tetrahedra. Air was thought to consist of octahedra since that was the only remaining Platonic solid. A little later, a fifth Platonic solid, the dodecahedron, was discovered, and this led to the proposal that there might be a fifth element or "quintessence," which also became known as ether.

Although the notion that elements are made up of Platonic solids is regarded as incorrect from a modern point of view, it is the origin of the very fruitful notion that macroscopic properties of substances are governed by the structures of the microscopic components of which they are comprised. These "elements" survived well into the Middle Ages and beyond, augmented with a few others discovered by the alchemists, the precursors of modern-day chemists. One of the many goals of the alchemists seems to have been the transmutation of elements. Not surprisingly, perhaps, the particular transmutation that most enticed them was the attempt to change the base metal lead into the noble metal gold, whose unusual color, rarity,

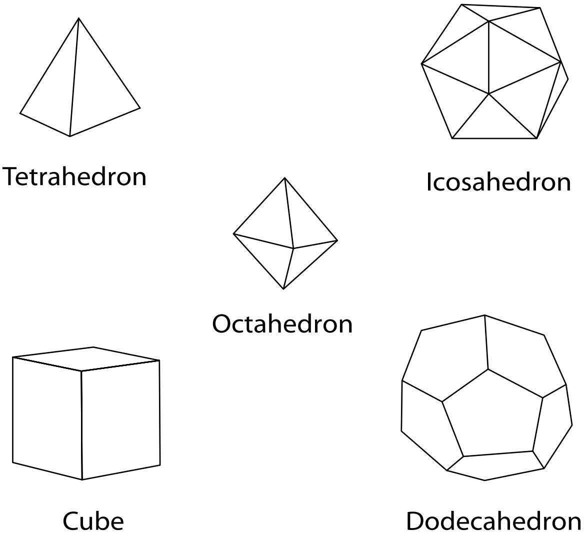
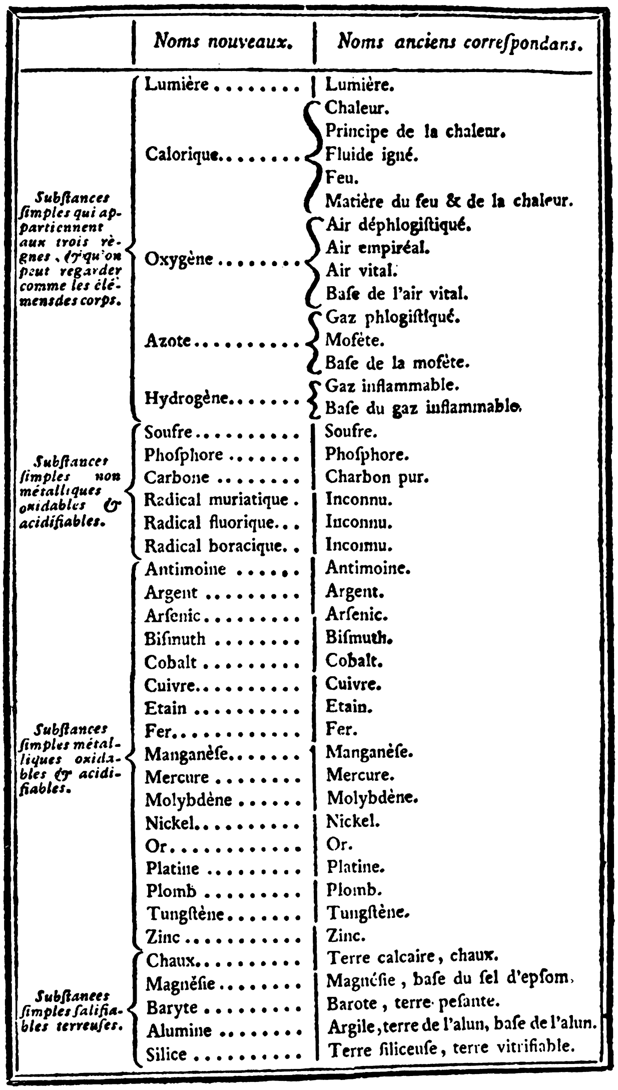


FIGURE 1.1 The five Platonic solids. O. Benfey, Precursors and Cocursors of the Mendeleev table: The Pythagorean Spirit in Element Classification, courtesy *Bulletin for the History of Chemistry*, 13-14, 60–66, 1992-93, figure from p. 60 (by permission).

and chemical inertness have made it one of the most treasured substances since the dawn of civilization.

The earliest understanding of the term "element" among the Greek philosophers was of a "tendency" or "potentiality" that gave rise to the observable properties of the element. This rather subtle distinction between the abstract form of an element and its observable form has been all but forgotten in modern times. It has nonetheless served as a fundamental guiding principle to such noted contributors to the periodic system as Dmitri Mendeleev, its major discoverer.

According to most textbook accounts, chemistry began in earnest only when it turned its back on alchemy and on this seemingly mystical understanding of the nature of elements. The triumph of modern science is generally regarded as resting on direct experimentation and the adoption of an empiricist outlook, which holds that only that which can be observed should count. Not surprisingly, therefore, the more subtle and perhaps more fundamental sense of the concept of elements was rejected. For example, Robert Boyle and Antoine Lavoisier both took the view that an element should be defined by an appeal to empirical observations, thus denying the role of abstract elements.[1] They recommended that an element should be defined as a material substance that has yet to be broken down into any more fundamental components by chemical means. In 1789, Lavoisier published a list of 33 simple substances or elements according to this empiricist criterion (figure 1.2).[2]



	Noms nouveaux.	*Noms anciens correſpondans.*
Subſtances ſimples qui appartiennent aux trois règnes, & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofète. Baſe de la mofète.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobalt	Cobalt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

FIGURE 1.2
List of 33 simple substances compiled by Lavoisier. *Traité Elémentaire de Chimie*, Cuchet, Paris, 1789, p. 192.

Gone were the ancient elements of earth, water, air, and fire, which had by now been shown to consist of simpler substances.[3]

Many of these substances would qualify as elements by modern standards, while others, such as *lumière* (light) and *calorique* (heat), are certainly no longer regarded as elements.[4] Rapid advances in techniques of separation and characterization of chemical substances over the forthcoming years would help chemists expand and refine this list. The important technique of spectroscopy, which measures the emission and absorption spectra of various kinds of radiation, would eventually yield a very accurate means by which each element could be identified through its unique "fingerprint." In modern times, we recognize 94 naturally occurring elements, and it has even been possible to extend the range of the elements beyond those that occur naturally.[5]

The Discovery of the Elements

The story of the discovery of the elements is a fascinating one and has been the subject of at least one classic account.[6] A time line for the discoveries is given in table 1.1. This story is not systematically addressed in the present book, although references to predictions and discovery of elements are made throughout.[7]

TABLE 1.1
Discovery time line for the elements and approximate dates of contributions from major chemists and physicists connected with the periodic system.

Antiquity	Au, Ag, Cu, Fe, Sn, Pb, Sb, Hg, S, C	
Middle Ages	As, Bi, Zn, P, Pt	
1700		
1710		
1720		
1730	Co	
1740		
1750	Ni, Mg	
1760	H	
1770	N, O, Cl, Mn, Ba	
1780	Mo, W, Te, Zr, U	Lavoisier
1790	Ti Y, Be	
1800	V, Nb, Ta, Rh, Pd, Os, Ir, Ce	Dalton, Avogadro
	K, Na, B, Ca, Sr, Ru, Ba	Davy
1810	I, Th, Li, Se, Cd	
1820	Si, Al, Br	Döbereiner
1830	La	
1840	Er	Gmelin
1850		Cannizzaro
1860	Cs, Rb, Tl, In, He	Mendeleev, Lothar Meyer
1870	Ga, Ho, Yb, Sc, Tm	
1880	Gd, Pr, Nd, Ge, F, Dy	
1890	Ar, He, Kr, Ne, Xe, Po, Ra, Ac	Ramsay, Rayleigh
1900	Rn, Eu, Lu	Thomson
1910	Pa	Lewis, van den Broek, Moseley
1920	Hf, Re, Tc, Ma	Bohr, Pauli, Schrödinger
1930	Fr	
1940	Np, At, Pu, Cm, Am, Pm, Bk	Seaborg

Table 1.1
(*Continued*)

1950	Cf, Es, Fm, Md, No
1960	Lr, Rf, Db
1970	Sg
1980	Bh, Mt, Hs
1990	Ds, Rg, Cn, Fl
2000	Lv, Og, Mc, Ts
2010	Nh

Compiled by the author.

There have been a number of major episodes in the history of chemistry when half a dozen or so elements were discovered almost at once, or within a period of a few years. Of course, some elements, such as iron, copper, gold, and other metals, have been known since antiquity. Indeed, historians and archeologists refer to certain epochs in human history as the Iron Age or the Copper Age. The alchemists added several more elements to the list, including sulfur, mercury, and phosphorus. In relatively modern times, the discovery of electricity enabled chemists to isolate many of the more reactive elements that, unlike copper and iron, could not be obtained by heating their ores with carbon. The English chemist Humphry Davy seized upon the use of electricity or, more specifically, electrolysis to isolate as many as 10 elements, including calcium, barium, magnesium, sodium, and chlorine.[8]

Following the discovery of radioactivity and nuclear fission, and the development of techniques in radiochemistry, it became possible to fill the remaining few gaps in the periodic table. The last gap to be filled was that corresponding to element 43, which became known as technetium from the Greek *techne*, meaning artificial or manufactured. It was "manufactured" in the course of some radiochemical reactions that would not have been feasible before the advent of nuclear physics. More recently, it was claimed that the Noddacks may in fact have synthesized element 43 as they claimed, although this attempted rehabilitation has been refuted.[9]

The most recent spate of elemental discoveries is also based on technological developments, involving the production and harnessing of beams of pure atoms or pure elementary particles such as neutrons. These particles can be fired at each other with great precision to achieve nuclear fusion reactions and to thereby create new elements with extremely high atomic numbers. One of the initiators of this field was the American chemist Glenn Seaborg, who first synthesized plutonium in 1943 and went on to head research teams that were responsible for the synthesis of 10 transuranium elements.

Names and Symbols of the Modern Elements

Part of the appeal of the periodic table derives from the individual nature of the elements and from their names.[10] The chemist and concentration camp survivor

Primo Levi began each chapter of his much-acclaimed book *The Periodic Table*[11] with a vivid description of an element such as gold, lead, or oxygen. The book itself is about his relations and acquaintances, but each anecdote is motivated by Levi's love of a particular element.[12] More recently, the well-known neurologist and author Oliver Sacks wrote a book called *Uncle Tungsten*, in which he told of his boyhood fascination with chemistry and in particular the periodic table.[13]

During the many centuries over which the elements have been discovered, many different themes have been used to select their names.[14] Just reading a list of the names of elements can conjure up episodes from Greek mythology. Promethium, element 61, takes its name from Prometheus, the god who stole fire from heaven and gave it to human beings, only to be punished for this act by Zeus.[15] The connection of this tale to element 61 seems to be the extreme effort that was needed to isolate it, just as the task performed by Prometheus was difficult and dangerous. Promethium is one of the very few elements that was not thought to occur naturally on the earth. It was initially obtained as a decay product from the fission of another element, uranium.

Planets and other celestial bodies have been used to name some elements. For example, palladium, which was discovered in 1803, is named after Pallas, or the second asteroid that was itself discovered just one year earlier in 1802. Helium is named after *helios*, the Greek name for the sun. It was first observed in the spectrum of the sun in 1868, and it was not until 1895 that it was first identified in terrestrial samples.

Many elements derive their names from colors. Cesium is named after the Latin color *caesium*, which means gray-blue, because it has prominent gray-blue lines in its spectrum. The yellow-green gas chlorine comes from the Greek word *khloros*, which denotes the color yellow-green.[16] The salts of the element rhodium often have a pink color, and this explains why the name of the element was chosen from *rhodon*, the Greek for rose. In cases of more recently synthesized elements, their names come from those of the discoverer or a person whom the discoverers wish to honor. This is why we have bohrium, curium, einsteinium, fermium, gadolinium, lawrencium, meitnerium, mendeleevium, nobelium, roentgenium, rutherfordium, seaborgium and, most recently, oganesson.[17]

A large number of elements' names have come from the place where their discoverer lived, or wished to honor: americium, berkelium, californium, darmstadtium, europium, francium, germanium, hassium, nihonium, polonium, gallium, hafnium, moscovium, lutetium, rhenium, ruthenium, scandium and tennessine. Yet other element names are derived from geographical locations connected with minerals in which they were found. This category includes the remarkable case of four elements named after the Swedish village of Ytterby, which lies close to Stockholm. Erbium, terbium, ytterbium, and yttrium were all found in ores located around this village, while a fifth element, holmium, was named after the Latin for Stockholm.

The naming of the later trans-uranium elements is a separate story in itself, complete with nationalistic controversies and, in some cases, acrimonious disputes over who first synthesized the element and should therefore be accorded the honor of selecting a name for it. In an attempt to resolve such disputes, the International Union of Pure and Applied Chemistry (IUPAC) decreed that the elements should be named impartially and systematically with the Latin numerals for the atomic number of the element in each case. Element 105, for example, would be known as un-nil-pentium, while element 106 would be un-nil-hexium. But more recently, after much deliberation over the true discoverers of some of these later superheavy elements, IUPAC has returned the naming rights to the discoverers or synthesizers who were judged to have established priority in each case. Instead of their impersonal Latin names, elements 117 and 118, for example, are now called tennessine and oganesson, respectively.[18]

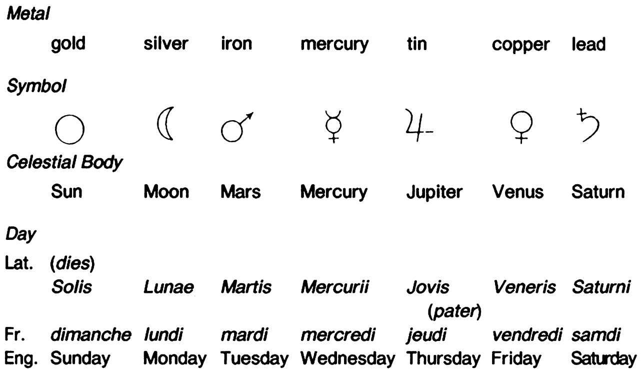
Seaborgium is a particularly interesting case, since for many years the committee did not approve of the choice of the American chemist Glenn Seaborg's name, even though he had been responsible for the synthesis of about 10 new elements, including number 106. Their official reason seems to have been an old rule that required that no element could be named after a person still living.[19] Following much campaigning by chemists in the United States and other parts of the world, Seaborg was finally granted his element while he was still alive.

Another curious case concerns the German chemist Otto Hahn, whose name was unofficially given to the element hahnium, only to be removed later and changed to the name dubnium after the place where several trans-uranium elements were synthesized. Meanwhile, an element has been named after Hahn's one-time colleague Lise Meitner. To many observers, this is a just move since Hahn had been awarded the Nobel Prize for the discovery of nuclear fission while Meitner, who had participated in many of the crucial steps in the work, was denied the prize.[20]

The symbols that are used to depict each element in the periodic table also have a rich and interesting story. In alchemical times, the symbols for the elements often coincided with those of the planets from which they were named or with which they were associated (figure 1.3). The element mercury, for example, shared the same symbol as that of Mercury, the innermost planetary body. Copper was associated with the planet Venus, and both the element and the planet shared the same symbol.

When John Dalton published his atomic theory in 1805, he retained several of the alchemical symbols for the elements. These were rather cumbersome, however, and did not lend themselves easily to reproduction in articles and books. The modern use of simple letter symbols was introduced by the Swedish chemist Jacob Berzelius a little later, in 1813.

In the modern periodic table, a small minority of elements are represented by a single letter of the alphabet. These include hydrogen, carbon, oxygen, nitrogen,



Metal							
	gold	**silver**	**iron**	**mercury**	**tin**	**copper**	**lead**
Symbol							
	☉	☾	♂	☿	♃	♀	♄
Celestial Body							
	Sun	**Moon**	**Mars**	**Mercury**	**Jupiter**	**Venus**	**Saturn**
Day							
Lat.	**(*dies*)**						
	Solis	***Lunae***	***Martis***	***Mercurii***	***Jovis*** **(*pater*)**	***Veneris***	***Saturni***
Fr.	***dimanche***	***lundi***	***mardi***	***mercredi***	***jeudi***	***vendredi***	***samdi***
Eng.	**Sunday**	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**

FIGURE 1.3 Names and symbols of the ancient metals compared to names of celestial bodies and days of the week. V. Rignes, *Journal of Chemical Education*, 66, 731–738, 1989, p. 731 (by permission).

sulfur, and fluorine, which appear as H, C, O, N, S, and F, respectively.[21] Most elements are depicted by two letters, the first of which is a capital letter and the second a lowercase letter. This gives rise to such element symbols as Li, Be, Ne, Ca, and Sc, for lithium, beryllium, neon, calcium, and scandium, respectively. Some of these two-letter symbols are by no means intuitively obvious, such as Cu, Na, Fe, Pb, Hg, Ag, and Au, which are derived from the Latin names for the elements copper, sodium, iron, lead, mercury, silver, and gold.[22] Tungsten is represented by a W after the German name for the element, which is *wolfram*. In fact, for the first and probably the last time, there are no missing elements in the periodic table, although this situation will only persist until a new 8th period will begin when element 119 is synthesized.[23]

The Modern Periodic Table

The manner in which the elements are arranged in rows and columns in the modern periodic table, also called the medium-long form (figure 1.4), reveals many relationships among them. Some of these relationships are very well known, while others still await discovery. To take just one example, in the 1990s scientists discovered that the property of superconductivity, the flow of current with zero resistance, could be observed at relatively high temperatures of about 100 Kelvin. This discovery was partly serendipitous. When the elements lanthanum, copper, oxygen, and barium were combined together in a particular manner, the resulting compound happened to display high-temperature superconductivity. There followed a flurry of worldwide activity in an effort to raise the temperature at which the effect could be maintained. The ultimate goal was to achieve room-temperature superconductivity, which would allow technological breakthroughs such as levitating

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 1.4 The modern or medium-long form table.

trains gliding effortlessly along superconducting rails. One of the main guiding principles used in this quest was the periodic table of the elements. The table allowed researchers to replace some of the elements in the compound with others that are known to behave in a similar manner and then examine the effect on superconducting behavior. This is how the element yttrium was incorporated into a new set of superconducting compounds, to produce the compound $YBa_2Cu_3O_7$ with a superconducting temperature of 93K.[24] This knowledge, and undoubtedly much more, lie dormant within the periodic system, waiting to be discovered and put to good use.

The conventional periodic table consists of rows and columns. Trends can be observed among the elements going across and down the table. Each horizontal row represents a single period of the table. On crossing a period, one passes from metals such as potassium and calcium on the left, through transition metals such as iron, cobalt, and nickel, then through some semimetallic elements such as germanium, and on to some nonmetals such as arsenic, selenium, and bromine on the right side of the table. In general, there is a smooth gradation in chemical and physical properties as a period is crossed, but exceptions to this general rule abound and make the study of chemistry a fascinating and unpredictably complex field.

Metals themselves can vary from soft dull solids such as sodium or potassium to hard shiny substances such as chromium, platinum, and gold. Nonmetals, on the other hand, tend to be solids or gases, such as carbon and oxygen, respectively. In terms of their appearance, it is sometimes difficult to distinguish between solid metals and solid nonmetals. To the layperson, a hard and shiny metal may seem to be more metallic than a soft metal such as sodium. But in a chemical sense, elements that have the greater ability to lose electrons (lower ionization energies) are regarded as being the more metallic. Sodium is therefore regarded by chemists as being more metallic than such elements as iron or copper. The periodic trend from metals to nonmetals is repeated with each period, such that when the rows are stacked they form columns, or groups, of similar elements. Elements within a single group tend to share many important physical and chemical properties, although there are many exceptions.

The manner in which the groups in the modern periodic table are labeled is complicated and controversial. The groups, or columns, of main-group elements, which are also referred to as representative elements, lie on the extreme left and right of the modern periodic table. In the United States, these groups were generally labeled with Roman numerals from I to VIII, with the letter A sometimes added to differentiate them from transition metals or groups IB to VIIIB, which lie in the central portion of the table. However, in Europe the convention was different in that all groups are sequentially labeled from left to right as IA to VIIIA until one reached the group headed by copper, where the labeling becomes IB up to the noble gases, which were said to be in group VIIIB (figure 1.5).[25] Both of these systems used the same Roman numeral for each column, which, in the case of main-group elements, also denotes the number of outer-shell electrons.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	—	VIIIB	—	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
IA	IIA	IIIA	IVA	VA	VIA	VIIA	—	VIIIA	—	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
H																	**He**
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
Cs	**Ba**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
Fr	**Ra**	**Lr**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Nh**	**Fl**	**Mc**	**Lv**	**Ts**	**Og**

La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**
Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**

FIGURE 1.5 Diagram of conventional periodic table format with alternative numbering systems for groups: the more recent IUPAC system (top line), US system (second line), and European system (third line). Note that 3 columns are labeled as VIII in the US European system but each column has a distinct number in the IUPAC system.

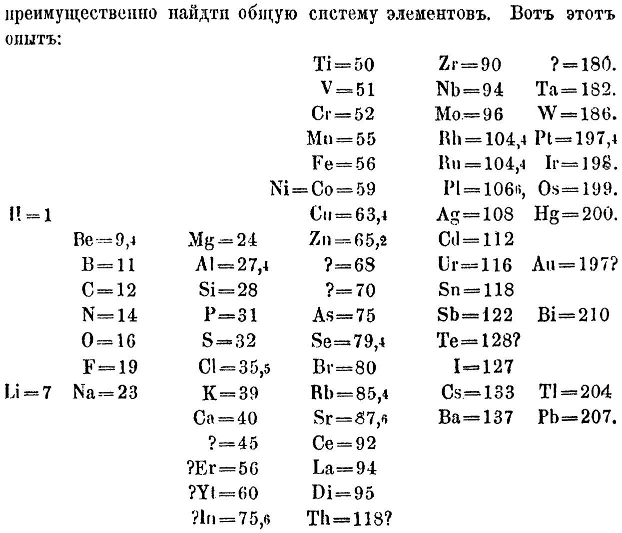
Given the confusion that these conventions have caused, there has been much attention directed at obtaining a unified system. In 1990, IUPAC recommended that groups should be sequentially numbered with Arabic numerals from left to right, as groups 1 to 18, without the use of the letters A or B. The unfortunate result of this proposal is that the direct correlation between the number of outer-shell electrons in the atoms of main-group elements and the group labels in the old US and European systems is lost. For example, the atom of oxygen has six outer-shell electrons and is said to be in group VI (followed by an A or a B) in the older systems, whereas in the IUPAC system it is considered to be in group 16. As a result, although many textbooks display the IUPAC recommendation on periodic tables, they generally fail to adhere to it when discussing the properties of the elements.[26]

This book mainly uses Roman numerals for the representative or main-group elements and refers to transition metal groups by the name of their first element. For example, group IVA in the US system (carbon, silicon, germanium, tin, and lead) is referred to as simply group IV. Meanwhile, group VIB in the US system (chromium, molybdenum, and tungsten) is referred to as the chromium group. Nevertheless, in some chapters the IUPAC system of numbering groups is used to avoid any possible confusion.

And so with this proviso, the extreme left of the table, group I contains such elements as the metals sodium, potassium, and rubidium. These are unusually soft and reactive substances, quite unlike what are normally considered metals, such as iron, chromium, gold, and silver. The metals of group I are so reactive that merely placing a small piece of one of them into pure water gives rise to a vigorous reaction that produces hydrogen gas and leaves behind a colorless alkaline solution.[27] The elements in group II include magnesium, calcium, and barium and tend to be less reactive than those of group I in most respects.

Moving to the right, one encounters a central rectangular block of elements collectively known as the transition metals, which include such examples as iron, copper, and zinc. In early periodic tables, known as short-form tables (figure 1.6), these elements were placed among the groups of what are now called the main-group elements. Several valuable features of the chemistry of these elements are lost in the modern table because of the manner in which they have been separated from the main body of the table, although the advantages of this later organization outweigh these losses.[28] To the right of the transition metals, in the medium-long form table, lies another block of representative elements starting with group III and ending with group VIII, the noble gases on the extreme right of the table.

Sometimes the properties a group shares are not immediately obvious. This is the case with group IV, which consists of carbon, silicon, germanium, tin, and lead. Here one notices a great diversity on progressing down the group. Carbon, at the head of the group, is a nonmetal solid that occurs in three completely different structural forms (diamond, graphite, and fullerenes)[29] and forms the basis of all



преимущественно найдти общую систему элементовъ. Вотъ этотъ опытъ:

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6,	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

FIGURE 1.6 Short-form table. The original Mendeleev's table published in 1869, D.I. Mnendeleev, Sootnoshenie svoistv s atomnym vesom elementov, *Zhurnal Russkeo Fiziko-Khimicheskoe Obshchestv,* 1, 60–77, 1869, table from p. 70.

living systems. The next element below, silicon, is a semimetal that, interestingly, may form the basis of artificial life, or at least "artificial intelligence," since it lies at the heart of all computers. The next element down, germanium, is a more recently discovered semimetal that was predicted by Mendeleev and later found to have many of the properties he foresaw. On moving down to tin and lead, one arrives at two metals known since antiquity. In spite of this wide variation among them, in terms of metal–nonmetal behavior, the elements of group IV nevertheless are similar in an important chemical sense in that they all display a maximum combining power, or valence, of 4.[30]

The apparent diversity of the elements in group VII is even more pronounced. The elements fluorine and chlorine, which head the group, are both poisonous gases. The next member, bromine, is one of the only two known elements that exist as a liquid at room temperature, the other one being the metal mercury.[31] Moving further down the group, one then encounters iodine, a violet-black solid element.[32] If a novice chemist were asked to group these elements according to their appearances, it is inconceivable that he or she would consider classifying together fluorine, chlorine, bromine, and iodine. This is one instance where the subtle distinction between the observable and the abstract sense of the concept of an element can be helpful. The similarity between them lies primarily in the nature of the abstract elements and not the elements as substances that can be isolated and observed.[33]

On moving all the way to the right, a remarkable group of elements, the noble gases, is encountered, all of which were first isolated just before, or at, the turn of

H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca															Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr															Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

FIGURE 1.7 Long-form periodic table.

the twentieth century.[34] Their main property, rather paradoxically, at least when they were first isolated, was that they lacked chemical properties.[35] These elements, which include helium, neon, argon, and krypton, were not even included in early periodic tables, since they were unknown and generally unanticipated. When they were discovered, their existence posed a formidable challenge to the periodic system, but one that was eventually successfully accommodated by extension of the table to include a new group, labeled group VIII or group 18 in the IUPAC system.

Another block of elements, found at the foot of the modern table, consists of the lanthanides and actinides that are commonly depicted as being literally disconnected. But this is just an apparent feature of this generally used display of the periodic system. Just as the transition metals are generally inserted as a block into the main body of the table, it is quite possible to do the same with the lanthanides and actinides. Indeed, many such long-form displays have been published. While the long-form tables (figure 1.7) give these elements a more natural place among the rest of the elements, they are rather cumbersome and do not readily lend themselves to conveniently shaped wall charts of the periodic system. Although there are a number of different forms of the periodic table, what underlies the entire edifice, no matter the form of its representation, is the periodic law.

The Periodic Law

The periodic law states that after certain regular but varying intervals the chemical elements show an approximate repetition in their properties. For example, fluorine, chlorine, and bromine, which all fall into group VII, share the property of forming white crystalline salts of general formula NaX with the metal sodium. This periodic repetition of properties is the essential fact that underlies all aspects of the periodic system.

This talk of the periodic law raises some interesting philosophical issues. First of all, periodicity among the elements is neither constant nor exact. In the generally used medium-long form of the periodic table, the first row has two elements, the second and third each contains eight, the fourth and fifth contain 18, and so on. This implies a varying periodicity consisting of 3, 9, 9, 19, and so on,[36] quite unlike the kind of periodicity one finds in the days of the week or notes in a musical scale. In these latter cases, the period length is constant, such as eight for the days of the week as well as the number of notes on a Western musical scale.

Among the elements, however, not only does the period length vary, but also the periodicity is not exact. The elements within any column of the periodic table are not exact recurrences of each other. In this respect, their periodicity is not unlike the musical scale, in which one returns to a note denoted by the same letter, which sounds like the original note but is definitely not identical to it, being an octave higher.

The varying length of the periods of elements and the approximate nature of the repetition have caused some chemists to abandon the term "law" in connection with chemical periodicity. Chemical periodicity may not seem as lawlike as the laws of physics, but whether this fact is of great importance is a matter of debate.[37] It can be argued that chemical periodicity offers an example of a typically chemical law, approximate and complex, but still fundamentally displaying lawlike behavior.[38]

Perhaps this is a good place to discuss some other points of terminology. How is a periodic table different from a periodic system? The term "periodic system" is the more general of the two. The periodic system is the more abstract notion that holds that there is a fundamental relationship among the elements. Once it becomes a matter of displaying the periodic system, one can choose a three-dimensional arrangement, a circular shape, or any number of different two-dimensional tables. Of course, the term "table" strictly implies a two-dimensional dimensional representation.[39] So, although the term "periodic table" is by far the best known of the three terms "law," "system," and "table," it is actually the most restricted.

Reacting Elements and Ordering the Elements

Much of what is known about the elements has been learned from the way they react with other elements and from their bonding properties. The metals on the left-hand side of the conventional periodic table are the complementary opposites of the nonmetals, which tend to lie toward the right-hand side. This is so because, in modern terms, metals form positive ions by the loss of electrons, while nonmetals gain electrons to form negative ions. Such oppositely charged ions combine together to form neutrally charged salts such as sodium chloride or calcium bromide. There are further complementary aspects of metals and nonmetals. Metal oxides or hydroxides dissolve in water to form bases, while nonmetal oxides or hydroxides dissolve in water to form acids. An acid and a base react together in a "neutralization" reaction to form a salt and water. Bases and acids, just like metals and nonmetals from which they are formed, are also opposite but complementary.[40]

Acids and bases have a connection with the origins of the periodic system since they featured prominently in the concept of equivalent weights, which was first used to order the elements. The equivalent weight of any particular metal, for example, was originally obtained from the amount of metal that reacts with a certain amount of a chosen standard acid. The term "equivalent weight" was subsequently generalized to denote the amount of an element that reacts with a standard amount of oxygen. Historically, the ordering of the elements across periods was determined by equivalent weight, then later by atomic weight, and eventually by atomic number.[41]

Chemists first began to make quantitative comparisons among the amounts of acids and bases that reacted together. This procedure was then extended to reactions between acids and metals. This allowed chemists to order the metals on a numerical scale according to their equivalent weight, which, as mentioned, is just the amount of the metal that combines with a fixed amount of acid. The concept of equivalent weights is, at least in principle, an empirical one since it seems not to rest on the theoretical assumption that the elements are ultimately composed of atoms.[42]

Atomic weights, as distinct from equivalent weights, were first obtained in the early 1800s by John Dalton, who indirectly inferred them from measurements on the masses of the relevant elements combined together. But there were complications in this apparently simple method that forced Dalton to make assumptions about the chemical formulas of the compounds in question. The key to this question is the valence, or combining power, of an element. For example, a univalent atom combines with hydrogen atoms in a ratio of 1:1; divalent atoms, such as oxygen, combine in a ratio of 2:1; and so on.

Equivalent weight, as mentioned above, is sometimes regarded as a purely empirical concept since it does not seem to depend upon whether one believes in the existence of atoms. Following the introduction of atomic weights, many chemists who felt uneasy about the notion of atoms attempted to revert to the older concept of equivalent weights. They believed that equivalent weights would be purely empirical and therefore more reliable. But as many authors have argued, most recently Alan Rocke, such hopes were an illusion since equivalent weights also rested on the assumption of particular formulas for compounds, and formulas are theoretical notions.

For many years, there was a great deal of confusion created by the alternative use of equivalent weight and atomic weight. Dalton himself assumed that water consisted of one atom of hydrogen combined with one atom of oxygen, which would make its atomic weight and equivalent weight the same, but his guess at the valence of oxygen turned out to be incorrect. Many authors used the terms "equivalent weight" and "atomic weight" interchangeably, thus further adding to the confusion. The true relationship between equivalent weight, atomic weight, and valency was clearly established only in 1860 at the first major scientific conference, which was held in Karlsruhe, Germany.[43] This clarification and the general adoption of consistent atomic weights cleared the path for the independent discovery of the periodic system by as many as six individuals in various countries, who each proposed forms of the periodic table that were successful to varying degrees. Each placed the elements generally in order of increasing atomic weight.[44]

The third, and most modern, of the ordering concepts mentioned above is atomic number. Once atomic number was understood, it displaced atomic weight as the ordering principle for the elements. No longer dependent on combining weights in any way, atomic number can be given a simple microscopic interpretation in terms of the structure of the atoms of any element. The atomic number of an element is given by the number of protons, or units of positive charge, in the nucleus of any of its atoms. Thus, each element on the periodic table has one more proton than the element preceding it. Since the number of neutrons in the nucleus also tends to increase as one moves through the periodic table, this makes atomic number and atomic weight approximately proportional, but it is atomic number that identifies any element. This is to say that atoms of any particular element always have the same number of protons, although they can differ in the number of neutrons they contain.[45]

Different Representations of the Periodic System

The modern periodic system succeeds remarkably well in ordering the elements by atomic number in such a way that they fall into natural groups, but this system can be represented in more than one way. Thus, there are many forms of the periodic table, some designed for different uses. Whereas a chemist might favor a form that highlights the reactivity of the elements, an electrical engineer might wish to focus on similarities and patterns in electrical conductivities.[46]

The way in which the periodic system is displayed is a fascinating issue, and one that especially appeals to the popular imagination. Since the time of the early periodic tables of John Newlands, Julius Lothar Meyer and Dmitri Mendeleev, there have been many attempts to obtain the "ultimate" periodic table. Indeed, it has been estimated that within 150 years of the introduction of Mendeleev's famous table of 1869, approximately 1000 different versions of the periodic table have been published. These include all kinds of alternatives, including three-dimensional tables, helices, concentric circles, spirals, zigzags, step tables, and mirror image tables.[47]

What is fundamental to all these attempts is the periodic *law* itself, which exists in only one form. None of the multitude of displays changes this aspect of the periodic system. Many chemists stress that it does not matter how this law is physically represented, provided that certain basic requirements are met. Nevertheless, from a philosophical point of view, it may still be relevant to consider the most fundamental representation of the elements, or the ultimate form of the periodic system, especially as this relates to the question of whether the periodic law should be regarded in a realistic manner or as a matter of convention.[48] The usual response that representation is only a matter of convention would seem to clash with the realist notion that there may be a fact of the matter concerning the points at which the repetitions in properties occur.[49]

Recent Changes in the Periodic Table

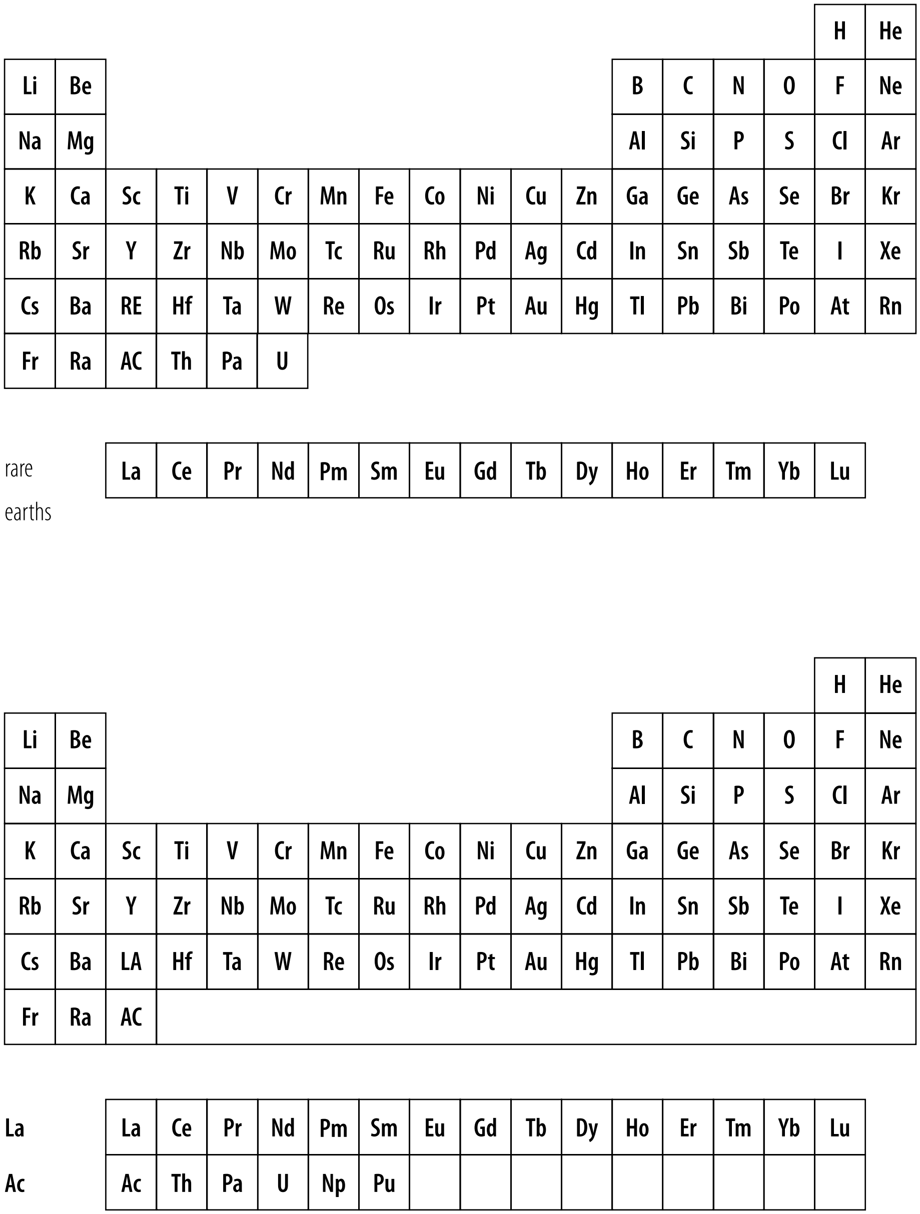
In 1945, Glenn Seaborg (figure 1.8) suggested that the elements beginning with actinium, number 89, should be considered as a series analogous to the lanthanides,

FIGURE 1.8
Glen Seaborg. Photo from Emilio Segrè Collection, by permission.

whereas it had previously been supposed that such elements would begin after element 92, or uranium (figure 1.9). Seaborg's new periodic table revealed an analogy between europium (63) and gadolinium (64) and the as yet undiscovered elements 95 and 96, respectively. On the basis of these analogies, Seaborg succeeded in synthesizing and identifying the two new elements, which were subsequently named americium and curium. A number of further trans-uranium elements have subsequently been synthesized.[50]

The standard form of the periodic table has also undergone some minor changes regarding the elements that mark the beginning of the third and fourth rows of the transition elements. Whereas older periodic tables show these elements to be lanthanum (57) and actinium (89), more recent experimental evidence and analysis have put lutetium (71) and lawrencium (103) in their former places.[51] It is also interesting to note that some even older periodic tables based on macroscopic properties had anticipated these changes.

These are examples of ambiguities in what may be termed secondary classification, which is not as unequivocal as primary classification, or the sequential ordering of the elements. In classical chemical terms, secondary classification corresponds to the chemical similarities between the various elements in a group. Meanwhile, in modern terms, secondary classification is explained by recourse to the concept of electronic configurations. Regardless of whether one takes a classical qualitative chemical approach or a more physical approach based on electronic configurations, secondary classification of this type is more tenuous than primary classification and cannot be established as categorically.[52] The way in which secondary classification, as defined here, is established is a modern example of the



																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	RE	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	AC	Th	Pa	U												

rare earths		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	LA	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	AC															

La		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac		Ac	Th	Pa	U	Np	Pu									

FIGURE 1.9 Pre-Seaborg (a) and post-Seaborg (b) periodic tables. RE denotes rare earth elements from 57–71 inclusive; LA, lanthanides ($Z = 57$–71); AC, actinides beginning with $Z = 89$, where Z is atomic number.

tension between using chemical properties or physical properties for classification. The precise placement of an element within groups of the periodic table can vary depending on whether one puts more emphasis on electronic configuration (a physical property) or its chemical properties. In fact, many recent debates on the placement of helium in the periodic system revolve around the relative importance that should be assigned to these two approaches.[53]

In recent years, the number of elements has increased well beyond 100 as the result of the synthesis of artificial elements. At the time of writing, every single element up to and including element 118 has been synthesized and officially named. This represents a unique moment in the history of the periodic table because all gaps and all periods in the table have been filled.[54] Such elements are typically very unstable, and only a few atoms are produced at any time. However, ingenious chemical techniques have been devised that permit the chemical properties of these so-called superheavy elements to be examined and allow one to check whether extrapolations of chemical properties are maintained for such highly massive atoms. On a more philosophical note, the production of these elements allows us to examine whether the periodic law is an exceptionless law, of the same kind as Newton's law of gravitation, or whether deviations to the expected recurrences in chemical properties might take place once a sufficiently high atomic number is reached. No surprises have been found so far, but the question of whether some of these superheavy elements have the expected chemical properties is far from being fully resolved. One important complication that arises in this region of the periodic table is the increasing significance of relativistic effects due to very rapidly moving electrons.[55] These effects cause the adoption of unexpected electronic configurations in some atoms and may result in equally unexpected chemical properties.

Understanding the Periodic System

Developments in physics have had a profound influence on the manner in which the periodic system is now understood. The two important theories in modern physics are Einstein's theory of relativity and quantum mechanics.

The first of these theories has had a limited impact on our understanding of the periodic system but is becoming increasingly important in accurate calculations carried out on atoms and molecules. The need to take account of relativity arises whenever objects move at speeds close to that of light. Inner electrons, especially those in the heavier atoms in the periodic system, can readily attain such relativistic velocities. It would be impossible to carry out an accurate calculation, especially on a heavy atom, without applying the necessary relativistic corrections. In addition, many seemingly mundane properties of elements such as the characteristic color of gold or the liquidity of mercury can best be explained as relativistic effects due to fast-moving inner-shell electrons.[56]

But it is the second theory of modern physics that has exerted by far the more important influence in attempts to understand the periodic system theoretically. Quantum theory was actually born in the year 1900, some 14 years before the discovery of atomic number. It was first applied to atoms by Niels Bohr, who pursued the notion that the similarities between the elements in any group of the periodic table could be explained by their having equal numbers of outer-shell electrons.[57] The very notion of a particular number of electrons in an electron shell is an essentially quantumlike concept. Electrons are assumed to possess only certain quanta, or packets, of energy, and depending on how many such quanta they possess, they lie in one or another shell around the nucleus of the atom.

Soon after Bohr had introduced the concept of the quantum to the understanding of the atom, many others developed his theory until the old quantum theory gave rise to quantum mechanics. Under the new description, electrons are regarded as much as waves as they are as particles. Even stranger is the notion that electrons no longer follow definite trajectories or orbits around the nucleus. Instead, the description changes to talk of smeared-out electron clouds, which occupy so-called orbitals.[58] The most recent explanation of the periodic system is given in terms of how many such orbitals are populated by electrons. The explanation depends on the electron arrangement or "configuration" of an atom, which is spelled out in terms of the occupation of its orbitals.[59]

The interesting question raised here is the relationship between chemistry and modern atomic physics and, in particular, quantum mechanics. The popular view reinforced in most textbooks is that chemistry is nothing but physics "deep down" and that all chemical phenomena, and especially the periodic system, can be developed on the basis of quantum mechanics. There are some problems with this view, however, which are considered in this book.

For example, in chapter 9 it is suggested that the quantum mechanical explanation for the periodic system is still far from perfect. This is important because chemistry books, especially textbooks aimed at teaching, tend to give the impression that our current explanation of the periodic system is essentially complete. This is just not the case, or so it will be argued.[60]

Molecular Tables

Another recent departure has been the invention of periodic tables designed to summarize the properties of compounds rather than elements. In 1980, Ray Hefferlin[61] produced a periodic system for all the conceivable diatomic molecules that can be formed between the first 118 elements. In order to represent this vast number of entries, Hefferlin used four three-dimensional blocks of varying sizes. His representation reveals that interatomic distances, spectroscopic frequencies, and molecular ionization energies are periodic properties. It also provided successful predictions regarding the properties of diatomic molecules.

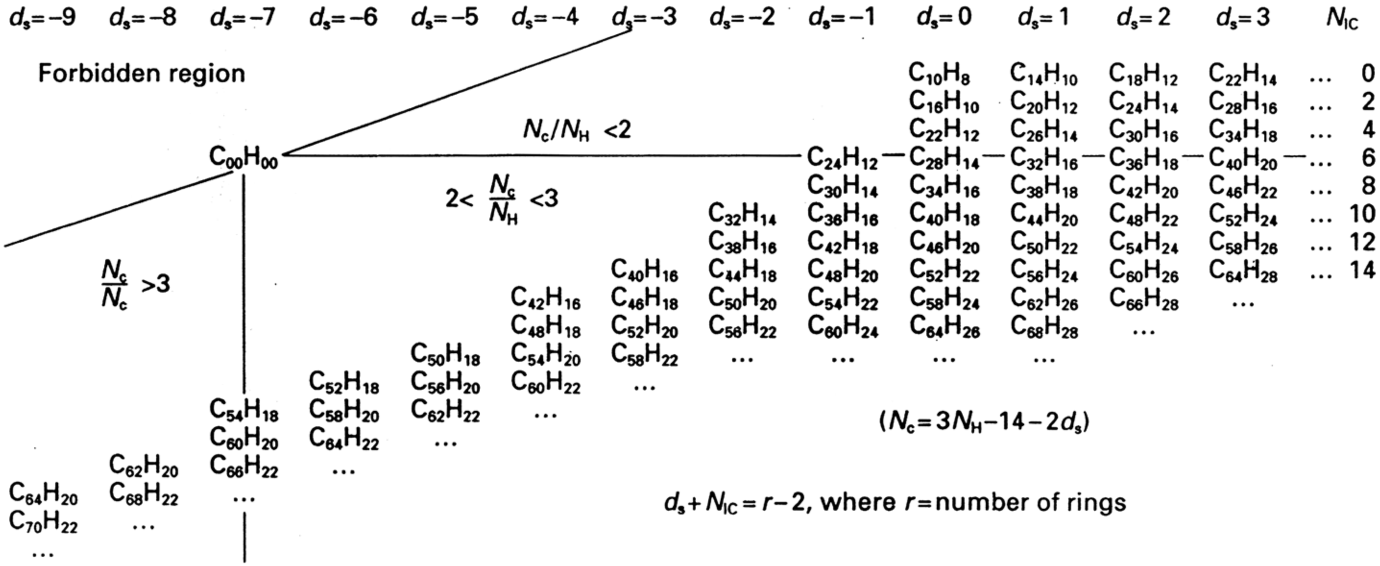


FIGURE 1.10 Dias's periodic classification of benzenoid aromatic hydrocarbons. J. Dias, Setting Benzenoids to Order, *Chemistry in Britain*, 30, 384–386, 1994,p. 384 (by permission).

Jerry Dias, a chemist at the University of Missouri–Kansas City, has devised a periodic classification of a class of organic molecules called benzenoid aromatic hydrocarbons, of which naphthalene, $C_{10}H_8$, is the simplest example (figure 1.10). By analogy with Johann Döbereiner's triads of elements, described in chapter 2, these molecules can be sorted into groups of three in which the central molecule has a total number of carbon and hydrogen atoms that is the mean of the flanking entries, both downward and across the table. This periodic scheme has been applied to making a systematic study of the properties of benzenoid aromatic hydrocarbons, which has led to predictions of the stability and reactivity of many of their isomers.

However, it is the periodic table of elements that has had the widest and most enduring influence. The periodic table ranks as one of the most fruitful and unifying ideas in the whole of modern science, comparable perhaps with Darwin's theory of evolution by natural selection. Unlike such theories as Newtonian mechanics, it has not been falsified by developments in modern physics but has evolved while remaining essentially unchanged. After evolving for 150 years through the work of numerous individuals, the periodic table remains at the heart of the study of chemistry. This is mainly because it is of immense practical benefit for making predictions about all manner of chemical and physical properties of the elements and possibilities for bond formation. Instead of having to learn the properties of the more than 100 elements, the modern chemist, or the student of chemistry, can make effective predictions from knowing the properties of typical members of each of the eight main groups and those of the transition metals and rare earth elements.

Having laid some thematic foundations and defined some key terms in chapter 1, I begin the story of the development of the modern periodic system, starting with its birth in the eighteenth and nineteenth centuries.

Notes

1. Lavoisier did not fully abandon the sense of elements as principles. For example, he regarded oxygen as one such principle.

2. There has been some debate concerning the precise criteria used by Lavoisier, given that several of the entries fail to meet his stipulation that simple substances are the final products of chemical analysis. R. Siegfried, B.J. Dobbs, Composition, A Neglected Aspect of the Chemical Revolution, *Annals of Science*, 29, 29–48, 1982.

3. With the exception of fire, which is a process rather than a substance.

4. Lavoisier's simple substances were defined in opposition to the classical view of the elements as abstract entities or principles. However, Lavoisier was not entirely consistent in that some of his simple substances appear to be more akin to the older principles. Discussion of this issue concerning the dual nature of elements is resumed in later chapters.

5. Until recently, it was believed that the elements technetium (atomic number 43) and promethium (atomic number 61) do not occur naturally. It is now known that trace amounts of these elements do occur in uranium ores. In addition, very small amounts of elements 93

and 94, or neptunium and plutonium, respectively, have also been detected, bringing the current total to 94 naturally occurring elements. For example, see D.C. Hoffman et al., The Detection of Plutonium-244 in Nature, *Nature*, 234 (5325), 132, 1971.

6. M.E. Weeks, H. Leicester, *The Discovery of the Elements*, 7th ed., *Journal of Chemical Education*, Easton, PA, 1968.

7. A full-length, meticulously researched book has also appeared on the elements that were first claimed but then wthdrawn or refuted. M. Fontani, M. Costa, M.V. Orna, *The Lost Elements*, Oxford University Press, New York, 2015.

8. In 2017 and again in 2019, I had the honor of delivering lectures on the periodic table at the Royal Institution (RI) in London, in the same auditorium where Davy lectured. In addition, the RI provided me with some of Davy's original samples of sodium and potassium to display during my presentations.

9. H.M. van Assche, The Ignored Discovery of Element Z = 43, *Nuclear Physics A*, A480, 205–214, 1988. See also note 4. F. Habashi, *Journal of Chemical Education*, 83, 213-213, 2006.

10. For a very informative article on the naming of compounds, from which I have drawn liberally for this section, see V. Ringnes, Origin of the Names of Chemical Elements, *Journal of Chemical Education*, 66, 731–738, 1989.

11. Primo Levi, *The Periodic Table*, 1st American ed., Schocken Books, New York, 1984.

12. Levi took his own life after surviving the holocaust and after writing several books, the best known of which remains *The Periodic Table*. He is believed to have acted out of survivor guilt.

13. O. Sacks, *Uncle Tungsten*, Alfred Knopf, New York, 2001.

14. The classic book on the discovery of the individual elements remains M.E. Weeks, H. Leicester, *The Discovery of the Elements*, 7th ed., Journal of Chemical Education, Easton, PA, 1968.

15. Other elements that take their names from mythology include vanadium (from Vanadis), niobium (from Niobe), and tantalum (from Tantalus).

16. The element names of rubidium, indium, and thallium are also derived from colors.

17. These scientists were all famous physicists, with the exception of Mendeleev and Seaborg, who were chemists.

18. The most recently approved names, at the time of writing, are nihonium (113), moscovium (115), tennessine (117), and oganesson (118).

19. The unofficial reason according to some observers is that certain members of the IUPAC committee objected to the idea of naming an element after the person who had synthesized such a deadly substance as plutonium, which was used in one of the atomic bombs dropped on Japan during the Second World War. At least that was the story told to me by the late Herb Kaesz, but it has been disputed by Willem Koppenol. In any case, element 118 was later named oganesson after the still-living Armenian-Russian scientist Yuri Oganessian.

20. Ruth Sime has written several articles and a book about the way in which the Nobel Prize committee overlooked Lise Meitner's work. R.L. Sime, *Lise Meitner: A Life in Physics*, University of California Press, Berkeley, 1996.

21. The others are boron (B), potassium (K), iodine (I), yttrium (Y), phosphorus (P), uranium (U), tungsten (W), and yttrium (Y). In all, 14 of the 118 currently named elements have a one-letter symbol.

22. These Latin names are *cuprum* (Cu), *natrium* (Na), *ferrum* (Fe), *plumbum* (Pb), *hydrargyrum* (Hg), *argentum* (Ag), and *aurum* (Au).

23. Another excellent and detailed account of the discovery and properties of all individual elements can be found in John Emsley, *Nature's Building Blocks: An A-Z Guide to the Elements*, Oxford University Press, Oxford, 2001.

24. The story of this development is mentioned by the discoverer of the compound, Paul Chu, in the article, Yttrium, *Chemical & Engineering News*, Special Issue on the Elements, September 8, 2003, p. 102.

25. The groups headed by copper and zinc are labeled IB and IIB, respectively, in both the US and European systems. Also note that in both systems three groups are collectively labeled VIIIB and VIIIA, respectively.

26. According to some observers, the IUPAC recommendation is really the European system in disguise since it numbers the groups sequentially from left to right regardless of whether they might be main-group elements or transition elements. The IUPAC numbering proposal also raises the question of what should be done if the rare earth elements are incorporated into the periodic table rather than being displayed as a footnote. This would strictly necessitate the numbering of all groups from 1 to 32.

27. With the exception of the first member of the group, lithium, which is rather unreactive, although it, too, forms an alkaline solution and even reacts vigorously with nitrogen when heated.

28. One example of a loss is the correspondence between the numbers in the group labels and the maximum oxidation state of the element in question.

29. Fullerenes, also known as buckyballs or buckminsterfullerenes, are the most recently discovered allotrope of carbon. The simplest such molecule contains a total of 60 carbon atoms arranged in the shape of a soccer ball, that is, a set of interlocking hexagons and pentagons. H. Aldersey-Williams, *The Most Beautiful Molecule*, John Wiley and Sons, New York, 1997.

30. But there are variations, in that the valence of 2 is increasingly the more predominant one as the group is descended. In the case of lead, compounds displaying a valence of 2 such as $PbCl_2$ are actually more stable than their 4-valent analogues such as $PbCl_4$ in this case.

31. However, in many countries cesium (melting point 28.5°C) and gallium (melting point 29.8°C) are also liquid at room temperature.

32. One further element in this group, astatine, has been discovered, but only a handful of atoms of it have ever been isolated. Its macroscopic properties, such as the color of the element, therefore remain unknown.

33. It is the abstract element that survives when elements form compounds, and there are more similarities among the compounds of the elements than in the isolated elements or elements as simple substances.

34. The actual dates are helium, 1895; neon, 1898; argon, 1894; krypton, 1898; xenon, 1898; and radon, 1900.

35. Hundreds of chemical compounds of krypton and xenon are now known. Only neon still resists all attempts at making them combine with other elements. Curiously, helium, which is generally believed to be the most noble of the noble gases, has now been shown to form a few compounds under high-pressure conditions. X. Dong et al., A Stable Compound of Helium and Sodium at High Pressure, *Nature*, 9, 440–445, 2017.

36. This way of counting period length counts the first element up to and including the element that represents the approximate repetition of the first one.

37. D.W. Theobald, Some Considerations on the Philosophy of Chemistry, *Chemical Society Reviews*, 5, 203–213, 1976.

38. The growing interest in the philosophy of chemistry, and specifically in the autonomy of chemistry, makes holding such views increasingly more plausible. E.R. Scerri, L. McIntyre, The Case for Philosophy of Chemistry, *Synthese*, 111, 213–232, 1997.

39. Whether or not a circular-shaped display would count as a table is debatable, although one sometimes encounters the term "circular periodic table." See the exhaustive

compilation of periodic tables assembled by Mark Leach at https://www.meta-synthesis.com/webbook/35_pt/pt_database.php.

40. Some time ago, in his highly popular book *The Tao of Physics*, Shambala, Berkeley, CA, 1975, F. Capra argued that modern physics shares many similarities with the Taoist philosophy of complementary opposites. It has been suggested that chemistry lends itself far more directly to such analogies. E.R. Scerri, The Tao of Chemistry, *Journal of Chemical Education*, 63, 100–101, 1986.

41. Much chemical history has been condensed into this sentence. The quantities used were first equivalent weight, then followed by a period of confusion in which atomic weights and equivalent weights (confusingly defined in several different ways) were used. After the Karlsruhe conference in 1860, atomic weights began to be used more exclusively, and finally atomic weight was replaced by atomic number as the main ordering criterion for the elements.

42. I am greatly oversimplifying the situation. As Alan Rocke and many others before him have argued, the use of equivalent weights in preference to atomic weights carried out by William Wollaston and others was motivated by the notion of avoiding theoretical assumptions as well as the existence of atoms. However, these chemists still needed to assume formulas for the compounds they were considering, and as a result, what they were calling equivalent weights were operationally equivalent to atomic weights. A. Rocke, Atoms and Equivalents, The Early Development of Atomic Theory, *Historical Studies in the Physical Sciences*, 9, 225–263, 1978; A.J. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State Press, Columbus, 1984.

43. Alan Rocke argues that this change was already in the air at the time and would have taken place regardless of the Karlsruhe meeting. A. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State Press, Columbus, 1984.

44. This is a generalization. E.g., it is not clear that Gustav Hinrichs's system followed this form of ordering. Also, some of the discoverers of the periodic system such as John Newlands began by using equivalent weights and later changed to using atomic weights.

45. The fact that atoms contain protons and neutrons also explains the concept of isotopes, which is of crucial importance in the story of the periodic table. Atoms of an element that differ in the number of neutrons they contain are said to represent different isotopes of that element. E.g., the element carbon has three most common isotopes: carbon-12, carbon-13, and carbon-14. Each of these contains six protons (which identifies them as carbon) but also six, seven, or eight neutrons, respectively. Each is said to have a different mass number given by the sum of protons and neutrons. The atomic weight of carbon is given by a weighted average of the masses of all the isotopes of the element, meaning an average, which takes account of how much of each isotope occurs in any given natural sample. Until atomic number was understood, the existence of isotopes made it difficult to fit some elements into a periodic scheme in what would appear to be the proper order based on their chemical properties.

46. E.g., see F. Habashi, A New Look at the Periodic Table, *Interdisciplinary Science Reviews*, 22, 53–60, 1997. This article presents a periodic table from the point of view of metallurgy. An interesting geologist's table can be found in L.B. Railsback, An Earth Scientist's Periodic Table of the Elements and Their Ions, *Geology*, 31, 737–740, 2003.

47. The author frequently receives articles, diagrams, and communications outlining new designs from passionate advocates of some particular version. He also regularly receives messages and letters from well-meaning enthusiasts asking for comments on new theories or representations concerning the periodic table.

48. The final comment is rather controversial, with many chemists believing that there is no one best representation. These authors consider representation to be a secondary issue,

which is dictated by convention. The present author takes issue with this view and supports a more realist interpretation whereby the grouping of troublesome elements such as hydrogen has an objective aspect and is not merely a manner of convenience. See E.R. Scerri, The Best Representation of the Periodic System: The Role of the $n + 1$ Rule and the Concept of an Element as a Basic Substance, in D. Rouvrary, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Science Studies Press, Bristol, UK, 2004, 143–160.

49. For a three-way debate on this point, see B. Hjorland, E. Scerri, J. Dupré, Forum: The Philosophy of Classification, *Knowledge Organization*, 38, 9–24, 2011.

50. P. Armbruster, F.P. Hessberger, Making New Elements, *Scientific American*, 72–77, September 1998. This article is followed by one on the history of the periodic system: E.R. Scerri, The Evolution of the Periodic System, *Scientific American*, 78–83, September 1998. A more recent article on the periodic table in the same magazine was E.R. Scerri, Cracks in the Periodic Table, *Scientific American*, June, 68–73, 2013.

51. W.B. Jensen, Classification, Symmetry and the Periodic Table, *Computation and Mathematics with Applications*, 12B, 487–509, 1986; H. Merz, K. Ulmer, Position of Lanthanum and Lutetium in the Periodic Table, *Physics Letters*, 26A, 6–7, 1967; D.C. Hamilton, M.A. Jensen, Mechanism for Superconductivity in Lanthanum and Uranium, *Physical Review Letters*, 11, 205–207, 1963; E.R. Scerri, W. Parsons, What Elements Belong in Group 3 of the Periodic Table? in E.R. Scerri, G. Restrepo, *Mendeleev to Oganesson*, Oxford University Press, New York, 2018, 140–151.

52. W.B. Jensen uses the terms "primary and secondary kinship," which should not be confused with the terms "primary and secondary classification" as used by the present author. A primary kinship as termed by Jensen results from secondary classification according to the terminology used in this book. W.B. Jensen, *Computation and Mathematics with Applications*, 12B, 487–509, 1986.

53. This is an important issue. The helium question is at the center of attempts to revolutionize the way in which the periodic system should be represented. See, e.g., Gary Katz, The Periodic Table: An Eight Period Table for the 21st Century, *The Chemical Educator*, 6, 324–332, 2001; E.R. Scerri, Presenting the Left-Step Table, *Education in Chemistry*, 42, 135–136, 2005.

54. Nevertheless, experiments are currently being conducted with the aim of synthesizing elements 119 and 120 and perhaps even heavier ones.

55. Strictly speaking, the electron is regarded as much as a delocalized wave as an orbiting particle, as explained a little later in the text. Use of the phrase "rapidly moving electrons" should therefore be regarded as a classical approximation in this context.

56. There are several relatively accessible articles on relativistic effects in atoms. L.J. Norrby, Why Is Mercury Liquid? *Journal of Chemical Education,* 68, 110–113, 1991; M.S. Banna, Relativistic Effects at the Freshman Level, *Journal of Chemical Education*, 62, 197–198, 1985; and D.R. McKelvey, Relativistic Effects on Chemical Properties, *Journal of Chemical Education*, 60, 112–116, 1983. For a more technical account, see P. Pyykkö, Relativistic Effects in Structural Chemistry, *Chemical Reviews*, 88, 563–594, 1988.

57. This idea was first proposed by the discoverer of the electron, J.J. Thomson.

58. The change in terminology from orbit to orbital is considered to be rather unfortunate by many, since the similarity in the two words does not begin to convey the radical change in the way that electron motion is regarded in quantum mechanics as compared with Bohr's old quantum theory.

59. The detailed evolution of the concept of electronic configurations is given in chapter 7. Also see Eric Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016.

60. I am not disputing the approximate nature of the current explanation of the periodic system, as B. Friederich seems to believe, but I am rather referring to the fact that the important $n + \ell$ rule has not yet been deduced from first principles. B. Friederich, *Foundations of Chemistry*, 6, 117–132, 2004; this is a response to the present author's article, Just How Ab Initio Is Ab Initio Quantum Chemistry? *Foundations of Chemistry*, 6, 93–116, 2004.

61. R. Hefferlin, H. Kuhlman, The Periodic System for Free Diatomic Molecules III, *Journal of Quantitative Spectroscopy and Radiation Transfer*, 24, 379–383, 1980. Hefferlin, who is named in the text, is also the author of a book on the subject: R. Hefferlin, *Periodic Systems of Molecules and Their Relation to the Systematic Analysis of Molecular Data*, Edwin Mellin Press, Lewiston, NY, 1989.

CHAPTER 2

QUANTITATIVE RELATIONSHIPS AMONG THE ELEMENTS AND THE ORIGINS OF THE PERIODIC TABLE

Elements within a vertical group on the periodic table share certain chemical similarities, but the modern periodic system is not derived purely from descriptive characteristics. If chemical similarities were the sole basis for their classification, there would be many cases where the order and placement of the elements would be ambiguous. The development of the modern periodic system began when it was recognized that there are precise numerical relationships among the elements. Its subsequent evolution has also involved contributions from physics, as described in subsequent chapters. But whereas the latter contributions drew on fundamental physical theories, the ones that are examined in this chapter do not share this aspect. Instead, they involved looking for patterns among the numerical properties, such as equivalent weight or atomic weight, associated with each element.[1]

Throughout its history, the development of the periodic table has required a delicate interplay between two contrasting approaches: discerning quantitative physical data, on one hand, and observing qualitative similarities among the elements as a form of natural history, on the other. Both approaches are essential, and the balance that has been struck between them has been of crucial importance at various stages in our story.

Quantitative Analysis

Whereas attention to qualitative aspects has always been an essential part of chemistry, the use of quantitative data has been a relatively new addition. The time when chemists began to pay attention to quantitative aspects of chemical reactions and chemical substances has been the source of much debate among historians. The traditional view has been that this step was taken by Antoine Lavoisier (figure 2.1), who is regarded as the founder of modern chemistry. The more recent historical account is that Lavoisier made few original contributions and that much of his fame lay in his abilities as an organizer and presenter of chemical knowledge.[2]

Nevertheless, Lavoisier was able to dispel some of the vagueness and confusion that dogged the field of chemistry as he found it. The confusion included the chaotic way in which substances were named, as well as the uncertain knowledge of weight changes accompanying chemical reactions. Prior to Lavoisier and his contemporaries, it was believed that when substances burned, they would release a substance called phlogiston. Although some substances do appear to lose weight when they are burned, many others show a gain in weight. Lavoisier used his considerable personal wealth to commission the making of the finest balances of his day, some of which could measure changes as accurately as one part in 600,000. As a result of his weighing experiments, Lavoisier succeeded in showing that substances that burned did not in fact give off phlogiston and, indeed, that the notion of phlogiston was redundant.[3] He also showed that what is essential for burning is the element oxygen, a substance that had previously been discovered by Swedish

FIGURE 2.1
Antoine Lavoisier. Photo from Edgar Fahs Smith Collection by permission.

chemist Carl Scheele and had been subjected to several earlier studies by the Englishman Joseph Priestley.[4]

Moreover, by accurately weighing reacting substances, Lavoisier was able to announce the law of conservation of matter, which states:

> *In every chemical operation, an equal quantity of matter*
> *exists before and after the operation.*

Lavoisier's emphasis on the quantification of chemistry also paved the way for the laws of chemical combination, which soon prompted John Dalton to develop his atomic theory. Returning to the revisionary accounts of Lavoisier, we note that it has been argued that a more significant development from the dismissal of phlogiston was the question of composition.

What Lavoisier achieved was a reversal of the compositional order that had been held by earlier chemists starting with Georg Stahl. In Lavoisier's chemistry, sulfur and phosphorus were simpler than their acids, thus displaying the opposite order than in the old chemistry. Contrary to the view of the old chemistry, metals were simpler than their calxes (oxides) according to Lavoisier. Likewise, hydrogen and oxygen were regarded as simpler than water in Lavoisier's compositional order, once again quite opposite the view held in the old chemistry.[5] Some historians regard Lavoisier's work as a culmination of the tradition begun a good deal earlier by the likes of Stahl on the question of chemical composition, rather than the start of a new tradition in chemistry.[6]

But perhaps Lavoisier's greatest contribution, particularly for our story, was one already mentioned briefly in chapter 1: Lavoisier was highly critical of the classical abstract element scheme of the Greeks and subsequent chemists. By adopting an empiricist approach, he attempted to eradicate any talk of abstract elements or principles in favor of elements as simple substances, which could be isolated and which could not be further decomposed. This antimetaphysical departure may have been just what was needed in chemistry at the time,[7] although Lavoisier did not succeed in completely dispensing with the need for elements as principles, as many authors have pointed out.[8]

Equivalent Weights

One of the next major developments, following along quantitative lines, was due to Jeremias Benjamin Richter, who between 1792 and 1794 published a set of quantities that later became known as equivalent weights (table 2.1). Richter first measured amounts of acids that combined with certain amounts of bases. He then extended this procedure to measuring the amount of some metals that combine with a certain fixed amount of acid, and thus he obtained an indirect measure of the relative amounts in which elements can combine together. This perhaps

TABLE 2.1
Richter's table of equivalent weights,
as modified by E. Fischer in 1802.

Base		*Acid*	
Alumina	525	Hydrofluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Sebaic	706
Lime	793	Muriatic	712
Soda	859	Oxalic	755
Strontia	1,329	Phosphoric	979
Potash	1,605	Sulfuric	1,000
Baryta	2,222	Succinic	1,209
		Nitric	1,405
		Acetic	1,480
		Citric	1,583
		Tartaric	1,694

E.G. Fischer, *Claude Louis Bethollet über die Gesetze der Verwandtschaft*, Berlin, 1802, table on p. 229.

marked the first time that the properties of the elements could be compared to each other on a simple numerical scale. This irresistible urge to find numerical patterns in nature would prove to be a powerful force in the development of the periodic table.

A Short Digression on Greek Atomism

The ancient Greek philosophers introduced atomism partly as a response to what they considered the awkward notion of infinity.[9] Zeno had introduced a famous paradox whose effect depended on the existence of infinity. According to the paradox, if a person needs to cover a certain distance between points A and B, he or she may do so by a series of steps. In the first step, the person covers half the distance. The second step involves covering half of the remaining distance and so on. Clearly, this process will continue ad infinitum since each time a step is taken it takes the person closer to the destination but never allows arrival. This paradox and many others like it depend on taking an infinite number of steps between points A and B.

If infinity is deemed to be unreal or unphysical, however, the problem appears to evaporate. One does indeed reach a destination because one cannot take an infinite number of steps. If distances are not infinitely subdivisible, there is no longer any paradox. But the Greek philosophers did not stop at denying infinite subdivisibility of distances. They applied the same denial to matter. They reasoned that a chunk of matter could likewise not be infinitely subdivided and that there would come a point in the subdivision when one had reached the smallest possible chunk of matter or *atomos*, meaning indivisible matter. Atoms of distance and atoms of matter were thus born of a philosophical desire to banish infinities from distances and from matter. But atomism of this kind remained a purely philosophical idea, and the Greek philosophers showed little inclination to perform experiments to support their notion.

Dalton's Atomic Theory

In 1801, Dalton (figure 2.2), a Manchester school teacher, published an article on meteorology, which was one of his main scientific interests. This work was to be the beginning of his reintroduction of atomic theory into science. Atomism had been proposed in ancient Greece, but it had subsequently been abandoned for about 2000 years, although the mention of atoms or small "particles" had not been entirely forgotten in scientific circles.[10] Indeed, Isaac Newton referred frequently to atoms, though not by name, including in the following passage, which Dalton knew well:

> It seems probable to me, that God in the beginning form'd matter in solid, massy, hard, impenetrable, moveable particles of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which he form'd them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them,

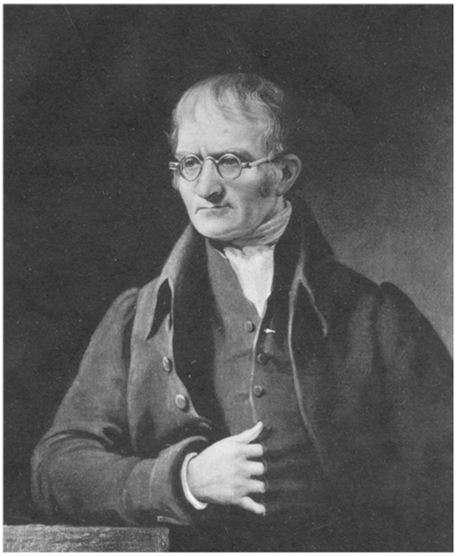


FIGURE 2.2
John Dalton. Photo from Edgar Fahs Smith Collection by permission.

> even so very hard, as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in the first creation.[11]

But in spite of Newton's notions on the quantification of chemistry, expressed in other passages, little more had been achieved in the field apart from the work of Lavoisier and others using the balance to try to understand chemical reactions, and Richter's little known work on equivalent weights. Lavoisier had taken a firmly empiricist[12] approach of ignoring the possible existence of unobservable atoms and focusing on elements as the final stages of chemical analysis of substances. Dalton rejected this position and embraced a realistic conception in which atoms actually exist and have particular sizes and weights.

Dalton's ideas on atomism can be summarized under three main points. First, he assumed that all matter was composed of atoms that were indestructible and nonchangeable, thus denying the possibility of the transmutation of elements. Dalton thus belonged to the new chemical tradition that consciously distanced itself from the alchemical doctrine of transmutation. Dalton was not the only one to do so, but he provides an interesting contrast to Robert Boyle, for example, who 150 years earlier also did important quantitative work in chemistry while at the same time being steeped in alchemy, as recent scholarly work has shown.

Second, and contrary to many of his contemporaries, who believed strongly in the unity of all matter, Dalton thought that there were as many different kinds of atoms as there were elements.[13] Finally, Dalton suggested that the weights of atoms would serve as a kind of bridge between the realm of microscopic unobservable atoms and the world of observable properties. But atomic weight is not necessarily the same as an equivalent weight, an issue raised in chapter 1 that will be revisited here.

Historians have traced the precise origin of Dalton's ideas to his research into the nature of the air, which had been found to consist of a mixture of gases. At the time, it was not understood why the various component gases of air did not separate out according to their different densities. In broad terms, Dalton reasoned that if gases consisted of tiny particles, or atoms, they would be more likely to form a mixture than if they consisted of continuous fluids. This argument is plausible if one accepts that continuous fluids cannot intermingle to the extent that tiny isolated particles can. It is also clear that part of Dalton's motivation for supporting an atomic theory lay in Newton's view that like particles should repel each other. According to this view, the different gases in the air intermingled rather than forming separate strata because particles of each gas would move away from each other to fill the available space, ignoring the particles of the other gases in the space.[14]

It is interesting to examine briefly how Dalton arrived at the values of atomic weights of the elements shown in table 2.2.[15] For example, he referred to Lavoisier's data on the composition of water, namely, 85% oxygen and 15% hydrogen. Assuming a formula of HO, Dalton calculated the weight of an oxygen atom to be 85/15 = approximately 5.5, by taking the weight of a hydrogen atom

Table 2.2
Part of an early table of atomic and molecular weights published by Dalton.

Element	*Weight*
Hydrogen	1
Azot	4.2
Carbon (charcoal)	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Nitrous gas	9.3
Ether	9.6
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2

Adapted from J. Dalton, *Memoirs of the Literary and Philosophical Society of Manchester,* 2(1), 207, 1805, table on p. 287. (Azot is the old name for nitrogen.)

as unity. Similarly, Dalton obtained a value for the nitrogen atom by drawing on William Austin's data showing that ammonia consists of 80% nitrogen and 20% hydrogen. Again, Dalton assumed the formula of this compound to be of the binary form NH.[16]

Dalton also suggested that the gases in the air diffused into one another because the particles were of different sizes, but he soon realized that it was the different weights of these particles, and not their sizes, that was the key feature in determining how gases would combine. In a paper published in 1803, he estimated the relative atomic weights of a number of different elements. The publication associated with this work represents the first ever list of atomic weights. Eventually, systems of classification would begin to be developed in which atomic weight would replace equivalent weight as the chief criterion by which elements were arranged, but this process was to take a period of about 60 years. Table 2.2 shows an early set of atomic and molecular weights, in modern terms, published by Dalton in 1805.

Another important consequence of Dalton's hypothesis that matter consists of atoms was that it provided an explanation of the long recognized law of constant proportion. As Richter had pointed out, when any two elements combine together, for example, hydrogen and oxygen, they always do so in a constant ratio of their masses. This fact can be understood if one assumes that a certain precise number of atoms of one element combine with a particular number of atoms of the other element. According to this view, macroscopic observations summarized in the law of constant proportion represent a scaled-up version of millions of such atomic combinations. If, on the other hand, matter did not consist of atoms but could be infinitely subdivided, it is not clear why oxygen and hydrogen, or any other elements, should always react together in the same particular ratio of masses.[17]

Meanwhile, others had made observations concerning the combination of masses of any two elements in more than one compound. It had been realized that if A reacts with B to form more than one compound, the various amounts of B that react with a fixed amount of A bear a simple whole number ratio to each other. Dalton carried out further experiments on this relationship, and as a result of his work, this, too, became regarded as a law of chemical combination (the law of multiple proportions) and one that his atomic hypothesis could readily explain. On the atomic hypothesis, the law of multiple proportions results from the fact that, for example, one oxygen atom can combine with one atom of carbon to form a compound, and in addition, two atoms of oxygen can combine with one atom of carbon to form a different compound. The ratio of amounts of oxygen combining with a fixed amount of carbon is therefore the simple ratio of 2 to 1. These two compounds are carbon monoxide and carbon dioxide, respectively.

At first, Dalton's concept of atomic weight did not improve the prospects of classifying the elements, since there were problems involved in calculating this quantity. While the equivalent weights introduced by Richter[18] at least appeared to have a clear experimental basis, Dalton's atomic weights, and those published by several of his contemporaries, seemed to be more theoretical, although this difference later turned out to be an illusion. The determination of atomic weights depended on assuming a particular formula for a compound and formulas could not yet be verified experimentally. The case of water provides a good example. One gram of hydrogen always reacts with approximately 8 grams of oxygen,[19] and thus the equivalent weight of oxygen is given as 8 grams relative to that of hydrogen. What Dalton did was assume that hydrogen and oxygen occur as individual atoms and that they combine at the atomic level, which thereby accounts for the macroscopic facts about the combination of specific volumes of hydrogen and oxygen. The problem is that unless the formula of water is known, this assumption can tell us nothing about the relative weights of the atoms of hydrogen and oxygen since it is not known how many hydrogen atoms are combining with each oxygen atom. At this point, Dalton was forced to make a guess as to whether one atom of each element had combined together or whether it was two of hydrogen and one of oxygen, or perhaps vice versa, or any other ratio of atoms. Dalton based such choices on what he called the rule of simplicity, meaning that in the absence of additional information, he would assume the simplest possible ratio of 1:1.[20] Accordingly, he assumed the formula of water to be HO and determined the atomic weight of oxygen to be 8, just like its equivalent weight.

The question of finding the correct formulas for compounds was conclusively resolved a good deal later when the concept of valency, the combining power of a particular element, was clarified by the chemists Edward Frankland and Auguste Kekulé working separately. Hydrogen, for example, has a valence of 1, while the value for oxygen is 2. It follows that two atoms of hydrogen combine with one of oxygen. With this new knowledge, the relationship between atomic weight and equivalent weight could be stated simply:

$$\text{atomic weight} = \text{valence} \times \text{equivalent weight}$$

Since oxygen has a valence of 2 and its equivalent weight is 8, as many early chemists had determined, its correct atomic weight is therefore twice that number, or 16. The correct formula for water is H_2O and not HO, as Dalton had assumed.

Law of Definite Proportions by Volumes

Soon after Dalton began to publish articles on his atomic theory, experiments were performed by Alexander von Humboldt and Joseph Louis Gay-Lussac leading to what was termed a law of definite proportions by volumes.[21] These scientists experimented on forming water vapor by passing electric sparks through a mixture of oxygen and hydrogen. They found that whatever volume of oxygen reacted, it was necessary to use almost exactly twice the volume of hydrogen to within ± 0.19%. They also noted that the volume of water vapor formed was almost identical to the volume of hydrogen initially used. Thus:

$$2 \text{ volumes of hydrogen} + 1 \text{ volume of oxygen} \rightarrow 2 \text{ volumes of water vapor}$$

They were able to extend this finding of whole number ratios to several other reactions involving gases. For example:

$$3 \text{ volumes of hydrogen} + 1 \text{ volume of nitrogen} \rightarrow 2 \text{ volumes of ammonia}$$

$$2 \text{ volumes of carbon monoxide} + 1 \text{ volume of oxygen} \rightarrow \\ 2 \text{ volumes of carbon dioxide}$$

Gay-Lussac summarized these results in a new law announced in 1809, which stated:

> The volumes of gases entering into chemical reaction and the gaseous products are in a ratio of small integers.

Recall that Dalton's main idea was that matter was composed of indivisible elementary atoms of fixed characteristic weight. Their combination in simple numbers gave rise to compound atoms and accounted for chemical laws such as the law of constant composition and the law of multiple proportions. However, when it came to Gay-Lussac's law, Dalton's original idea was unable to explain the observations summarized in equations such as those above. Consider the first equation again:

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of water[22]

Using the benefit of hindsight, we can easily appreciate the cause of the problem. Since one volume of oxygen was combining with two volumes of hydrogen, this implied that particles of oxygen must have been dividing.

But this idea contradicts the very heart of Dalton's notion that the smallest particles of any element are supposed to be indivisible. Dalton's own reaction to Gay-Lussac's law was to question the data and to repeat the experiments. This led to his claiming that the ratios were not in fact as simple as reported by von Humboldt and Gay-Lussac. Nevertheless, the simple ratio continued to be reproduced by others and has passed the test of time. Dalton could have accepted the existence of molecules of elements composed of two or more atoms of an element while still holding that such a body represented the simplest chemical unit that retains the properties of the element in question, but he failed to do so.

Meanwhile, Gay-Lussac suggested the very plausible notion that the appearance of small integers relating volumes in the reactions implied that *e*qual *v*olumes of gases contained *e*qual *n*umbers of particles, EVEN.[23] The step of reconciling Dalton's ideas on the existence of atoms with Gay-Lussac's law was taken by the Italian scientist Amedeo Avogadro in 1811. The crucial new ingredient introduced by Avogadro was that, contrary to what had previously been believed, the ultimate particles of a gas were not necessarily composed of single atoms but could equally well be assemblies of two or more atoms. Such assemblies or molecules could thus form the ultimate particles of any gaseous element.

Avogadro's idea was to provide the solution to Gay-Lussac's law while still maintaining the existence of Dalton's ultimate particles, although such particles could now be diatomic molecules, which were capable of subdivision. Unfortunately, Avogadro's resolution was understood by very few chemists at the time and had to wait a further 50 years before it became firmly established by fellow Italian chemist Stanislao Cannizzaro. It was Cannizzaro who helped to bring order to the prevailing confusion regarding atomic weights, as described in chapter 3.

Prout's Hypothesis

A rather remarkable fact began to emerge after values of equivalent weights and atomic weights had been published. Apart from some exceptions, many of the equivalent weights and atomic weights appeared to be approximate whole number multiples of the weight of hydrogen. To some chemists, this stubborn fact pointed against Dalton's idea of distinct elements and represented support for the essential unity of all the elements. More specifically, it suggested that all the elements, or their atoms, might be multiples of atoms of hydrogen. This would mean that there was really only one kind of matter, which could occur in different states of combination.

The first person to articulate this view clearly was the Scottish physician William Prout. Since the equivalent weights and atomic weights of the elements were nowhere near being exact multiples of each other, Prout rounded them off to the nearest whole number and gave hydrogen a value of 1. Such was the seductive lure of the Pythagorean tradition for seeking simple ratios, and it was this conviction that allowed Prout to ignore the apparent discrepancies as seen in the nonintegral values of the weights of some elements.

Prout's first articles on this subject appeared anonymously in Thomas Thomson's *Annals of Philosophy* along with a rather modest disclaimer:

> The author of the following essay submits it to the public with the greatest diffidence; for though he has taken the utmost pains to arrive at the truth, he has not such confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame.[24]

In his second paper on this hypothesis, Prout added,

> If the views we have ventured to advance be correct, we may almost consider the *protyle* of the ancients to be realized in hydrogen; an opinion by-the-bye, not altogether new.[25]

The term "protyle" refers to an underlying primary matter, which some Greek philosophers believed to be the basis of all matter. The word itself is derived from *proto-hyle*, or "first stuff." Whereas for Dalton there were numerous distinct kinds of basic substances or elements, those with a more unitary view of matter, such as Prout, could not accept such a notion.[26] Prout's mention of the fact that his idea was not entirely new in the above quotation has given rise to much speculation by subsequent commentators. It seems to be agreed that he may well have obtained at least part of his idea from the writings of the English chemist Humphry Davy, who believed that many elements literally contained hydrogen. In 1808, Davy had written,

> The existence of hydrogen in sulphur is fully proved, and we have no right to consider a substance, which can be produced from it in such large quantities, merely as an accidental ingredient.[27]

Experiments inspired by Prout's hypothesis provided an increasingly accurate set of atomic weights, which could then be used to try to order the elements in the periodic system. Many of the pioneers of the periodic system, including Wolfgang Döbereiner, Leopold Gmelin, Max Pettenkofer, Jean-Baptiste André Dumas, and Alexandre Émile Béguyer De Chancourtois, were very interested in Prout's hypothesis, and it figured prominently in their ideas regarding classification of the elements.

Although Prout's hypothesis fared well initially, at least in England, where it was supported by Thomas Thomson, who had first published the work, it would fall in and out of favor for years to come. In 1825, Jöns Jacob Berzelius, who would become one of the most influential chemists of his era, compiled a set of improved atomic weights that refuted Prout's hypothesis.[28] For example, the values in table 2.3 are the atomic weights of some selected elements according to Dalton and Berzelius, respectively.[29]

Berzelius objected to the practice of rounding off atomic weights to obtain whole numbers, which was common among supporters of the hypothesis; he had the following rather harsh words to say about Thomson, who as mentioned above was a supporter of Prout:

> This investigator belongs to that very small class from which science can derive no advantage whatever . . . and the greatest consideration which contemporaries can show to the author is to treat this work as if it had never happened.[30]

In 1827, the German chemist Leopold Gmelin, undaunted by such warnings, proceeded to round off even Berzelius's values, such as the ones shown in table 2.3, and to thereby reassert support for Prout's hypothesis:

> It is surprising that in the case of many substances the combining [equivalent] weight is an integral multiple of that of hydrogen, and it may be a law of nature that the combining weights of all other substances can be evenly divided by that of the smallest of them all.[31]

As other chemists continued to improve the accuracy of the atomic weights for existing elements and determined values for new elements, much of their data seemed to point away from the hypothesis. At the same time, however, new coincidences emerged where the more accurate atomic weights of some key elements were found to be very close to exact ratios.[32] This in part inspired Jean-Baptiste Dumas, another influential French chemist, to revive Prout's hypothesis once again in 1857. These ratios included those for carbon, oxygen, and nitrogen:

TABLE 2.3
Comparison of some of Dalton's and Berzelius's atomic weights.

	H	*N*	*Mg*	*Na*
Dalton (1810)	1	5	10	21
Berzelius (1827)	1.06	14.2	25.3	46.5

Based on J. Dalton, *A New System of Chemical Philosophy*, R. BickerstaY, Manchester & London, part II, 1810, p. 248; J.J. Berzelius, *Lehrbuch der Chemie*, 2nd ed., Arnold, Dresden, vol. 3, part I, 1827, p. 112.

$$C : H \sim 12 : 1$$
$$O : H \sim 16 : 1$$
$$N : H \sim 14 : 1$$

Throughout this period, however, there was one unavoidable obstacle to the ready acceptance of Prout's hypothesis, which no amount of rounding or remeasuring would redress. This was the fact that the atomic weight of chlorine stubbornly refused to change from its measured value of about 35.5, thus providing an apparently clear contradiction to the hypothesis.

Then, in 1844 the French chemist Charles Marignac made the ingenious suggestion of considering the basic unit of measurement as half the mass of the hydrogen atom, thus making chlorine almost exactly 71 times the weight of this unit. In 1858, Dumas took a further step and suggested a quarter of the weight of hydrogen as the basic unit, which made even more elements fall into line with the revised form of Prout's hypothesis. Of course, there is no limit to how small one might make the basic unit, but the smaller it became, the more the strength of Prout's original hypothesis appeared to be weakened.

The person who did the most to refute Prout's hypothesis was the Belgian Jean Servais Stas, who began his researches into atomic weight determination in 1841 by writing, "I will say it loudly. When I undertook my researches I had an almost absolute faith in the correctness of Prout's hypothesis."[33]

Almost 25 years later, however, after measuring the atomic weights of numerous elements with as yet unheard of precision, Stas drastically changed his opinion and declared, "One must consider Prout's hypothesis as pure illusion."[34] Whereas he had originally thought that an increased precision in atomic weight determination would reveal integral multiples of the value for hydrogen, it served only to show the opposite. Far too many elements showed weights that were clearly not whole number multiples of the weight of hydrogen.

Despite the apparent problems with Prout's hypothesis, it remained true that many elements, far more than chance seemed to allow, had atomic weight values that are almost integral. As Lord William Rayleigh wrote in 1901, long after Prout's hypothesis seemed to have fallen by the wayside,

> The atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence. . . . [T]he chance of any such coincidence being the explanation is not more than one in one thousand.[35]

The explanation for why some elements did not show integral atomic weights had to await the discovery of isotopes. Eventually, it would be understood that the elements whose values on a hydrogen scale are close to being whole numbers are those that exist only in one form or whose other forms, or isotopes, occur only in very small amounts.[36] By contrast, many elements showed values that differed markedly from whole numbers, such as chlorine (35.46), copper (63.57), zinc (65.38), and mercury (200.6). Their atomic weights were not exact or even close to exact multiples of hydrogen's weight because they occur as mixtures of several isotopes that are present in comparable amounts.

So Prout's hypothesis turned out to be incorrect in that the elements are not composites of hydrogen according to their atomic weights, and yet there is a sense in which his idea can be said to have now been vindicated by modern physics. In terms of numbers of protons, the nuclei of all the elements are indeed composites of the nucleus of the hydrogen atom, which contains just a single proton. Nevertheless, even at the time it was first proposed, Prout's hypothesis proved to be very fruitful, because it encouraged the determination of accurate atomic weights by numerous chemists who were trying to either confirm or refute it.[37] From the point of view of Karl Popper's philosophy of science, this all makes perfect sense. A useful scientific idea need not necessarily be correct, but it is essential that it should be refutable in the light of experimental evidence.

Döbereiner Discovers Triads

Just as the examination of atomic weight data led to Prout's hypothesis, so it was to produce another fruitful philosophical principle, that of triads. This development originated with the German chemist Johann Döbereiner, who was active in the city of Jena in the early 1800s. Döbereiner became interested in the emerging study of stoichiometry, the study of proportions in chemical reactions, and became an early adherent of the newly developed theory of chemical atomism. He was the first to notice the existence of various groups of three elements, subsequently called triads, which showed chemical similarities and which displayed an important numerical relationship: namely, that the equivalent weight, or atomic weight, of the middle element is the approximate mean of the values of the two flanking elements in the triad.

In 1817, Döbereiner found that if certain elements were combined with oxygen in binary compounds, a numerical relationship could be discerned among the equivalent weights of these compounds. Thus, when oxides of calcium, strontium, and barium were considered, the equivalent weight of strontium oxide was approximately the mean of those of calcium oxide and barium oxide.[38] The three elements in question, strontium, calcium, and barium, were said to form a triad:[39]

$$\begin{aligned} \mathrm{SrO} &= (\mathrm{CaO} + \mathrm{BaO})/2 = 107 \\ &= (59 + 155)/2 \end{aligned}$$

Though Döbereiner was working with weights that had been deduced with the relatively crude experimental methods of the time, his values compare rather well with current values for the triad:[40]

$$104.75 = (56 + 153.5)/2$$

Döbereiner's observation had little impact on the chemical world at first but later became very influential. He is now regarded as one of the earliest pioneers of the development of the periodic system. What is not often reported in modern accounts is that Döbereiner considered the possibility that the middle element of his triad might actually be a mixture of the other two elements in question and that his observations might support the notion of transmutation among the three elements.[41]

Very little happened regarding triads until 12 years later, in 1829, when Döbereiner added three new triads. The first involved the element bromine, which had been isolated in the previous year. He compared bromine to chlorine and iodine, using the atomic weights obtained earlier by Berzelius:

$$\mathrm{Br} = (\mathrm{Cl} + \mathrm{I})/2 = (35.470 + 126.470)/2 = 80.470$$[42]

The mean value for this triad is reasonably close to Berzelius's value for bromine of 78.383. Döbereiner also obtained a triad involving some alkali metals, sodium, lithium, and potassium, which were known to share many chemical properties:

$$\mathrm{Na} = (\mathrm{Li} + \mathrm{K})/2 = (15.25 + 78.39)/2 = 46.82$$[43]

In addition, he produced a fourth triad:

$$\mathrm{Se} = (\mathrm{S} + \mathrm{Te})/2 = (39.239 + 129.243)/2 = 80.741$$[44]

Once again, the mean of the flanking elements, sulfur and tellurium, compares well with Berzelius's value of 79.5 for selenium.

Döbereiner also required that, in order to be meaningful, his triads should reveal chemical relationships among the elements as well as numerical relationships. On the other hand, he refused to group fluorine, a halogen, together with chlorine, bromine, and iodine, as he might have done on chemical grounds, because he failed to find a triadic relationship among the atomic weights of fluorine and those of these other halogens. He was also reluctant to take the occurrence of triads among dissimilar elements, such as nitrogen, carbon, and oxygen, as being in any sense significant, even though they did display the triadic numerical relationship.

Suffice it to say that Döbereiner's research established the notion of triads as a powerful concept, which several other chemists were soon to take up with much effect. Indeed, Döbereiner's triads, which would appear on the periodic table grouped in vertical columns, represented the first step in fitting the elements into a system that would account for their chemical properties and would reveal their physical relationships.[45]

Before the correct relationship between atomic and equivalent weights had been discovered, some chemists regularly referred to atomic weights as equivalents and vice versa. To make matters worse, even when the same terminology was used by any given two chemists, there was still disagreement as to actual values, since different workers used various standards. In addition, the methods for obtaining atomic weights were applicable only to gases. Initially, it was not possible to estimate the atomic weights of liquids and solids, and this made it difficult to recognize periodic relationships, since on crossing a period one typically moves from solids to gases.

It is therefore not surprising that groups of similar elements in the periodic table were discovered long before periods involving dissimilar elements or, in other words, that vertical relationships were discovered before horizontal ones, in modern terms. Of course, there is a more immediate reason why groups were discovered long before periods: elements within groups share chemical properties, thus rendering their grouping intuitively obvious. Although this is quite true, what is being addressed here is the separate issue of the recognition of numerical relationships among elements in groups. The existence of the periodic table depends not only on chemical properties but also almost as much on numerical aspects and on physical principles, although the latter in particular raise certain philosophical questions concerning the reduction of chemistry.

Gmelin's Remarkable System

In 1843, a full 26 years before the publication of Dmitri Mendeleev's famous system of 1869, a much neglected and underrated periodic system was published (figure 2.3).[46] This was the work of Leopold Gmelin, the author of the rather voluminous *Handbuch der Chemie* and one of the most influential chemical writers of this time.[47]

Although Döbereiner is rightly regarded as the originator of the notion of triads, Gmelin also did much useful work in this area, and it was he who coined the term "triad." Like Döbereiner, Gmelin considered both chemical and numerical relationships when looking for triads, and he was able to extend his predecessor's work using improved atomic weights that had been unavailable to Döbereiner. For example, whereas Döbereiner had grouped magnesium together with the alkaline earths based on their chemical similarities, he was unable to find a triad relationship involving it and other alkaline earth elements. Gmelin, on the other hand, was able to discern the following relationship among magnesium, barium, and calcium, using his own newly obtained values for atomic weights, which he published in the same book in 1827:

$$(\mathrm{Mg} + \mathrm{Ba})/4 = \mathrm{Ca}$$
$$(12 + 68.6)/4 = 20.15\ (\mathrm{Ca} = 20.5)$$[48]

But let us now turn to the more remarkable aspects of Gmelin's system of 1843. From the existence of four unconnected triads discovered by Döbereiner, Gmelin

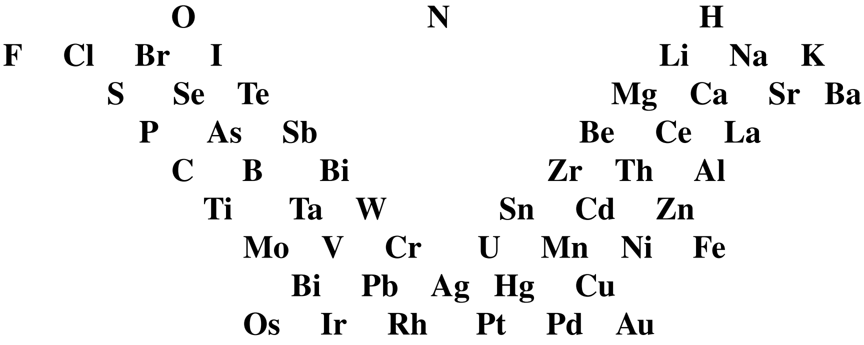


FIGURE 2.3 System of 1843. L. Gmelin, *Handbuch der anorganischen chemie* 4th ed., Heidelberg, 1843, vol. 1, p. 52.

was able to make a huge leap forward in obtaining a system based on triads consisting of as many as 55 elements. In addition, his system as a whole was essentially ordered according to increasing atomic weight. With this work, Gmelin succeeded in capturing the correct grouping of most of the then known main-group elements. Gmelin arranged his triads horizontally in the V-shaped schematic shown in figure 2.3.

Suppose we take the arms of Gmelin's V shape and make them lie flat, and then consider the arrangement obtained (figure 2.4). It is important to appreciate that this change does not alter Gmelin's table in any fundamental way but merely represents its contents. If atomic weights are introduced explicitly into the table, something that Gmelin did not do, a general decrease in this quantity in both wings of main-group elements is seen.

On removing all the elements in the central portion of figure 2.4, the entire table can be rotated by 90°, and all the columns can be stacked together, as shown in figure 2.5. What Gmelin's table achieves, granted this artistic license, is an essentially correct grouping of many of the current representative, or main-group, elements. Though he failed to arrange the transition metals and inner transition metals correctly, this can hardly be taken as a reason for thinking any less of his system, since problems with transition metals were common even in later, more mature periodic systems.

The fact that Gmelin could have produced such an arrangement of the main-group elements so early in the evolution of the periodic system, as shown in figure 2.5, is rather remarkable. In the case of groups I, II, IV, V, VI, and VII, *all* the elements included are shown in the correct order of increasing atomic weight going left to right. Boron and bismuth, which would have been placed incorrectly in group IV on moving from figure 2.4 to 2.5, have been omitted from 2.5. The only main-group misplacements appear to be nitrogen and oxygen, but Gmelin clearly recognizes that oxygen belongs with sulfur, selenium, and tellurium when he points out the following relationship, which also includes antimony:

O N H

F Cl Br I

S Se Te

P As Sb

C B Bi

Ti Ta W

Mo V Cr U Mn Ni Fe

Bi Pb Ag Hg Cu

Os Ir Rh Pt Pd Au

Sn Cd Zn

Zr Th Al

Be Ce La

Mg Ca Sr Ba

Li Na K

FIGURE 2.4 Flattened version of Gmelin's system.

H	**Li**		**C**			**F**
	Na	**Mg**		**P**	**S**	**Cl**
	K	**Ca**		**As**	**Se**	**Br**
		Sr		**Sb**	**Te**	**I**
		Ba				

FIGURE 2.5 Gmelin's table rotated, after removing the remaining 34 elements.

$$O = 8, S = 16, Se = 40, Te = 64, Sb = 129 = 1:2:5:8:16$$

Perhaps Gmelin's table cannot be properly called a periodic system, since it does not depict the well-known tendency of the elements to recur, that is, to show periodicity after certain regular intervals. Moreover, Gmelin's system does not *explicitly* arrange the elements in increasing order of atomic weight. But there may have been an implicit use of atomic weight ordering in Gmelin's system, since his placing of many of the triads side by side produces the correct order as found in subsequent more mature periodic systems.[49] It is also known that Gmelin was very interested in values of atomic weights, since in 1827 he produced an early list of atomic weights for as many as 45 elements.[50]

About 25 years before Mendeleev, Gmelin used his own rudimentary system of the elements to give overall structure and direction to his chemical textbook. He was thus possibly the first chemistry textbook author to do so. Although Mendeleev is usually credited with basing a textbook around the periodic system of the elements, he used an inductive approach, not presenting his system until the final chapter of the first volume of his textbook, even in later editions.[51] Gmelin, on the other hand, gives the system immediately on the very first page, at the start of volume 2 of his series, and the remainder of this volume is a detailed 500 or so page survey of the chemistry of 12 nonmetallic elements.[52]

Moreover, the order that Gmelin elects to follow in his presentation is dictated by the system itself. He begins with oxygen and hydrogen, two of the three elements at the head of his table. His following chapters discuss the chemistry of carbon and boron, which Gmelin placed together in the same group. He then discusses the chemistry of phosphorus, the only nonmetal in group V of the modern table apart from nitrogen. This is followed by chapters on sulfur and selenium, which are the nonmetals in what became group VI. After that comes a survey of the chemistry of all four of the then-known nonmetals in group VII of the modern periodic table.

Finally, the volume closes with the chemistry of nitrogen, the remaining one of the three elements that Gmelin placed at the head of his system of elements. Apart from the misplacement of boron along with carbon,[53] in what would correspond to the modern group IV, Gmelin gives a systematic survey of most of the important nonmetals in the order of groups IV, V, VI, and VII, from the perspective of the mature periodic system, which emerged only with the work of Mendeleev in 1869. This, I submit, suggests Gmelin's remarkable foresight and intuition, as does the way in which he uses his system to ground the presentation of the chemistry of these elements. Yet Gmelin's contribution to the classification of the elements has not been sufficiently appreciated by historians of chemistry, or even historians of the periodic system.[54] Johannes van Spronsen, the author of the respected scholarly book on the history of the periodic system, mentions Gmelin's remarkable table of 1843, but does so somewhat dismissively:

> In 1843 Gmelin also tried to find a relationship existing between all elements. This however, meant demoting the atomic weight. . . . The elements oxygen, nitrogen and hydrogen, for which he apparently could find no homologues, form the basis for his classification.[55]

But van Spronsen appears not to notice that Gmelin did in fact correctly classify at least one of these elements, oxygen, with sulfur, selenium, and tellurium.[56] Perhaps Gmelin's system should no longer be regarded as something of a footnote to Döbereiner's discovery of the existence of triads but rather as an important discovery of almost equal stature.

A Qualitative Intermission

In order to appreciate the advances that were made by considering quantitative properties of the elements, it is necessary to also consider what was known in qualitative terms at the time that the periodic system was beginning to ferment. One obvious way to do this is to consult some chemistry textbooks of the period, since they serve as the repository of the chemical knowledge known at the time. For the sake of brevity, I describe the set of textbooks written by Gmelin, whose successive editions would eventually give rise to a very influential set of books on inorganic chemistry.[57] It is not possible to divorce quantitative aspects altogether, given that, as noted above, Gmelin recognized triads based on atomic weights and even appears to have ordered the elements to some implicit extent on their atomic weights. Nevertheless, the influential series of books by Gmelin was primarily a summary of all the qualitative knowledge on the elements available at the time.

In volume 2 of his series, Gmelin gives a classification system for the elements that had been identified at the time (figure 2.2). As he puts it, these are 61 "undecomposable ponderable bodies," of which 12 are nonmetallic and 49 are metallic.

These elements are arranged in groups horizontally according to their chemical and physical properties, with the more electronegative elements on the left and the more electropositive ones on the right side. Gmelin does not specify more precisely what determines the order of the elements from left to right. One can only suppose that it might be degrees of electronegativity.[58] For example, the halogens are arranged in a row starting with fluorine, which is the most electronegative of them, followed, in decreasing order of electronegativity, by chlorine, bromine, and iodine.

The halogens represent a family of elements whose group similarities became apparent almost as soon as they were isolated and, in the case of fluorine, even before its isolation. Considering these elements in historical order, chlorine was first discovered by Carl Scheele in 1774, although he believed that it contained oxygen. It was first isolated in 1810 by Davy, who was the first to recognize that it was an element. That same year saw the first isolation of iodine by Bernard Courtois, followed by bromine in 1826 by Antoine Balard. Fluorine had not yet been isolated at the time that Gmelin was writing, although it had been recognized as an element. It was finally isolated in 1886, sometime after Gmelin devised his system. However, it had been studied in compound form by many chemists, including Davy, Gay-Lussac, and Lavoisier, all of whom experimented on one of its most common compounds, hydrofluoric acid.

Writing in 1843, Gmelin devoted a total of 123 pages to these four elements (chlorine, iodine, bromine, and fluorine) alone. Starting with the least electronegative of them, he discusses the reactions of iodine with water and oxygen and the existence of various oxides of iodine, such as IO_5 and IO_7. This is followed by discussion of the reactions of iodine with a number of other elements, namely, hydrogen, boron, phosphorus, sulfur, selenium, and the other halogens. Gmelin proceeds to discuss the chemistry of bromine and chlorine, which give analogous reactions with all the same elements as iodine and which form analogous acids with a few minor exceptions.[59]

In the case of fluorine, the same pattern of reactivity is described with a few more exceptions. These more noticeable differences might be explained by the fact that the element had not yet been isolated, so it was not as easy to examine its reactions with all the elements as had been possible in the case of iodine, bromine, and chlorine.[60] Overall, the well-established similarity among chlorine, bromine, and iodine would explain why fluorine was one of the first set of elements grouped together as a chemically significant triad by Döbereiner. The differences with fluorine might explain why it was frequently omitted from triads or extended triads, called tetrads.

Another nonmetallic group of elements given by Gmelin in his classification consists of sulfur, selenium, and tellurium. As in the case of the halogens, Gmelin does not specifically discuss the analogies among these elements, but the reader is left in no doubt by a study of the detailed chemistry of the elements in Gmelin's text. Sulfur and selenium are discussed, one after the other, over a total of 94 pages, only 20 of which are devoted to selenium. As in the case of the halogens, the chemical similarities, at least for sulfur and selenium, are abundantly obvious. They include reaction with oxygen, acid formation, and reaction with hydrogen, phosphorus, sulfur, bromine, chlorine, and a number of metals. Although the element tellurium is clearly grouped with sulfur and selenium, Gmelin does not discuss its chemistry along with these latter two elements. This would seem to indicate some ambiguity in the classification of the element tellurium. In fact, the chemistry of tellurium is delayed until volume 4, when it finally makes an appearance following descriptions of the reactions of the group consisting of phosphorus, antimony, and bismuth. It would appear that Gmelin is ambivalent about the classification of tellurium. Whereas in the system shown in figure 2.2 it is included among the elements of what would become group VI in the modern periodic table, in discussing the detailed chemistry of the element, Gmelin appears to contradict his earlier choice. The chemical and physical properties of tellurium are discussed in the context of the elements of the modern group V, along with phosphorus, arsenic, and antimony.[61]

The element nitrogen, which heads the modern group V, is separated from all these elements, however, and is discussed at a very early stage in volume 2. Recall that nitrogen, along with hydrogen and oxygen, is shown at the head of the system with no particular group membership.[62]

Turning to Gmelin's grouping of metals, we encounter a group containing lithium, sodium, and potassium. As well as being one of the triads discovered by Döbereiner, the chemical grouping of the elements is virtually inescapable. The elements are all soft, have a low density, and react with water to form alkaline solutions.[63] The analogies among them are remarkable given that all of them react, without fail, with oxygen, boron, carbon, phosphorus, sulfur, selenium, and the halogens, though to varying degrees.

Similarly, Gmelin summarizes the chemical similarities among another group of metals consisting of magnesium, calcium, strontium, and barium,[64] the last three of which had been recognized as the very first triad of elements by Döbereiner.[65] These elements are physically harder and less reactive than those of Gmelin's group consisting of lithium, sodium, and potassium. In modern terms, the major difference between these two groups of elements is that lithium, sodium, and potassium show a valence of 1, while magnesium, calcium, strontium, and barium show a valence of 2. Gmelin appears not to have recognized this feature, however, since the formulas he gives for all their oxides, for example, consist of one atom of the metal combined to one atom of oxygen.[66] It would seem that the qualitative differences alone between the members of the two groups sufficed to convince Gmelin and others that the elements concerned belonged in two different groups.

Pettenkofer's Difference Relationships

In 1850, at the University of Munich, Max Pettenkofer, another supporter of Prout's hypothesis, published an article dealing with numerical relationships among the equivalent weights of the elements. But unlike his predecessors, Pettenkofer did not focus on triads, believing that the findings by Döbereiner and others were due to mere chance. As an example, Pettenkofer pointed out that while the atomic weight of the middle member of the chlorine, bromine, and iodine triad was indeed the mean of the flanking elements, this was not the case in the chemically analogous triad of fluorine, chlorine, and bromine.

Nevertheless, Pettenkofer, too, created what essentially amounted to triads, and even larger groups of elements, although by a quite different approach. In the course of an examination of the data on the known elements, Pettenkofer realized that some series of chemically similar elements tended to show constant differences among their equivalent weights. He noted, for example, that the weights of lithium, sodium, and potassium differed by gaps of 16 units (table 2.4). As some authors remark, Pettenkofer thus failed to notice that this was tantamount to Döbereiner's recognition that the middle element has an equivalent weight that is the mean of the two flanking elements.

TABLE 2.4
Pettenkofer's atomic weight gaps.

	Li		*Na*		*K*
Equivalent weights	7		23		39
Differences		16		16	

Based on M. Pettenkofer, Ueber die regelmässigen Abstände der Aequivalenzzahlen der sogenannten einfachen Radicale, *Annalen der Chemie und Pharmazie*, 105, 187-202, 1858.

In some other series of elements, Pettenkofer pointed out that the differences in equivalent weights were a multiple of a certain number, such as 8 in the case of the alkaline earths and the oxygen group (table 2.5).

In taking these steps, Pettenkofer was already going beyond triads to considering larger series of elements. In the case of carbon, boron, and silicon, which were often grouped together in early classifications of the elements, as well as in the case of the halogens, the differences were factors of 5. In addition, there was another series, containing nitrogen, phosphorus, arsenic, and antimony, in which the differences involved factors of both 5 and 8, as shown in table 2.6.

On the basis of this theory of constant differences, and multiples of constant differences, Pettenkofer proposed the idea of calculating the equivalent weights for elements whose values would be difficult to measure otherwise. It is perhaps significant that Mendeleev some time later mentioned the name of Pettenkofer in his own articles as one of the few who had influenced his work on the periodic system. As is well known, Mendeleev made much use of predictions based on interpolations among atomic weights, and he also used interpolations to correct the atomic weights of already known elements. Given the work of such chemists as

TABLE 2.5
Pettenkofer's differences in atomic weights for alkaline earths and oxygen group.

	Mg		*Ca*		*Sr*		*Ba*
Equivalent weight	12		20		44		68
Differences		8		3(8)		3(8)	
	O		*S*		*Se*		*Te*
Equivalent weights	8		16		40		64
Differences		8		3(8)		3(8)	

Based on M. Pettenkofer, Ueber die regelmässigen Abstände der Aequivalenzzahlen der sogenannten einfachen Radicale, *Annalen der Chemie und Pharmazie*, 105, 187-202, 1858.

TABLE 2.6
Pettenkofer's atomic weight differences for the "nitrogen series".

	N		*P*		*As*		*Sb*
Equivalent weights	14		32		75		129
Differences		18		43		54	
		2(5)+8		7(5)+8		9(5)+8	

Based on M. Pettenkofer, Ueber die regelmässigen Abstände der Aequivalenzzahlen der sogenannten einfachen Radicale, *Annalen der Chemie und Pharmazie*, 105, 187-202, 1858.

Pettenkofer, it is clear that the idea of making such predictions did not originate with Mendeleev.[67]

Dumas's Contributions and His Revival of Transmutation

The year 1851 was a rather busy one for the famous French chemist Dumas, who published two important papers and delivered an influential public lecture in Ipswich, England, on the classification of the elements.[68] Throughout this work, Dumas drew attention to four triads—(S, Se, Te), (Cl, Br, I), (Li, Na, K), and (Ca, Sr, Ba)—but without mentioning Döbereiner as their original discoverer. Whereas the German chemist had suggested that the middle member of each triad might be a mixture of the two extreme elements, Dumas thought that the middle member was a compound of its flanking partners and offered this idea as support for Prout's hypothesis.

Dumas went as far as to suggest that transmutation might be possible among the elements in each triad and that research should be carried out to discover the mechanism of these possible transformations. He also took the fact that elements such as cobalt and nickel are often found associated together in nature as further evidence of the possibility of elemental transmutation. Interestingly, the English scientist Michael Faraday praised Dumas's public lecture and agreed that these findings suggested some form of transmutation. Faraday said:

> Thus we have here one of the many scientific developments of late origin, which tend to lead us back into speculations analogous with those of the alchemists . . . and now we find, after our attention has been led in that direction, that the triad of chlorine, bromine and iodine not only offers well-marked progression of certain chemical manifestations, but that the same progression is accordant with the numerical exponents of their combining weights. We seem here to have a dawning of a new light, indicative of the mutual convertibility of certain groups of elements, although under conditions which as yet are hidden from scrutiny.[69]

I draw attention to this passage because it reveals that at least some leading chemists appeared to continue to believe in this central alchemical doctrine long after alchemy had supposedly been abandoned.

Kremers Goes Horizontal

Peter Kremers, working in Koln, Germany, was one of the earliest chemists to begin to consider what would eventually form horizontal series of elements in the mature periodic systems of the future. He did this by examining the numerical

Table 2.7

Kremers's atomic weight differences for the oxygen series.

	O		*S*		*Ti*		*P*		*Se*
Equivalent wt.	8		16		24.12		32		39.62
Difference		8		≅ 8		≅ 8		≅ 8	

Based on P. Kremers, *Annalen der Physik und Chemie (Poggendorff)*, 85, 37, 246, 1852.

relationships among the atomic weights of elements with little in common. For example, he noted the regularity among a short series of elements that included oxygen, sulfur, titanium, phosphorus, and selenium shown in table 2.7.[70]

Kremers also discovered some new triads, such as

$$\mathrm{Mg} = \frac{\mathrm{O}+\mathrm{S}}{2},\ \mathrm{Ca} = \frac{\mathrm{S}+\mathrm{Ti}}{2},\ \mathrm{Fe} = \frac{\mathrm{Ti}+\mathrm{P}}{2}$$

From a modern standpoint, these triads may not seem to be chemically significant. There are two reasons for this seeming insignificance. The modern medium-long form of the periodic table fails to display secondary kinships among some elements. Sulfur and titanium both show a valence of 4, for example, though they do not appear in the same group in the medium-long form of the periodic table.[71] But it is not so far-fetched to consider them as being chemically analogous. Given the fact that both titanium and phosphorus commonly display valences of 3, this grouping, too, is not as incorrect as a modern reader may think. The second reason why one should not be too surprised by some of the less plausible triad groupings made by Kremers is that the notion of a triad had begun to take on a life of its own as distinct from chemical analogies. The aim had become one of finding triad relationships among the weights of the elements irrespective of whether or not this had a chemical significance. Mendeleev later described such activity among his colleagues as an obsession with triads, which he believed to have delayed the discovery of the mature periodic system.

But to return to Kremers: perhaps his most incisive contribution lay in the suggestion of a bidirectional scheme of what he termed "conjugated triads." Here, certain elements would serve as members of two distinct triads lying perpendicularly to each other,

Li 6.5	Na 23	K 39.2
Mg 12	Zn 32.6	Cd 56
Ca 20	Sr 43.8	Ba 68.5

Thus, in a more profound way than any of his predecessors, Kremers was comparing chemically dissimilar elements, a practice that would reach full maturity only with the tables of Julius Lothar Meyer and Mendeleev.

TABLE 2.8
Kremers's differences between calculated and observed atomic weight triads.

Triad (T)	*Middle element (M)*	*(T – M)/T*
K + Li/2	Na	–0.007
Ba + Ca/2	Sr	+0.010
Ag + Hg/2	Pb	+0.003
J + Cl/2	Br	+0.016
S + Se/2	Cr	+0.038
S + Te/2	Se	+0.017
Cr + Va/2	Mo	+0.035
P + Sb/2	As	+0.009

The headings for each column have been adapted from the original table, which uses different symbols. The modern symbol for vanadium is V rather than Va as in this table. J denotes iodine, or *jod* in German.

P. Kremers, *Annalen der Physik und Chemie (Poggendorff)*, 99, 58–63, 1856.

In 1856, Kremers mistakenly claimed that the divergences from exact values in the relationships among triads were caused by changes in temperature and that each triad would show an exact numerical relationship at a particular temperature. In the course of this research, he produced the table shown in table 2.8. One suspects that most people studying this table would have been seduced into thinking that the divergences were indeed very small and might well be spurious, thus further strengthening the notion of triads.

Supertriads

The most ambitious scheme of all involving triads was created by the 20-year-old Ernst Lenssen while he was working at an agricultural institute in Wiesbaden. In 1857, Lenssen published an article in which virtually all of the 58 known elements were arranged into a total of 20 triads, with the exception of niobium, which he could not fit into any triad (table 2.9).[72] Ten of his triads consisted of nonmetals and acid-forming metals, and the remaining 10 of just metals.

Lenssen also suggested further relationships involving groups of triads. Using the 20 triads in table 2.9, he was able to identify a total of seven enneads, or supertriads, in which the mean equivalent weight of each middle triad lies approximately midway between the mean weights of the other triads in a group of three triads (table 2.10). However, as the table shows, Lenssen was forced to combine his triads in a somewhat arbitrary order to achieve this goal. In addition, one supertriad involves just one element, hydrogen, rather than a triad of elements.

Table 2.9

The 20 triads of Lenssen.

			Calculated atomic weight	*Determined atomic weights*		
1	(K + Li)/2	= Na	= 23.03	39.11	23.00	6.95
2	(Ba + Ca)/2	= Sr	= 44.29	68.59	47.63	20
3	(Mg + Cd)/2	= Zn	= 33.8	12	32.5	55.7
4	(Mn + Co)/2	= Fe	= 28.5	27.5	28	29.5
5	(La + Di)/2	= Ce	= 48.3	47.3	47	49.6
6	Yt Er Tb			32	?	?
7	Th Norium Al			59.5	?	13.7
8	(Be + Ur)/2	= Zr	= 33.5	7	33.6	60
9	(Cr + Cu)/2	= Ni	= 29.3	26.8	29.6	31.7
10	(Ag + Hg)/2	= Pb	= 104	108	103.6	100
11	(O + C)/2	= N	= 7	8	7	6
12	(Si + Fl)/2	= Bo	= 12.2	15	11	9.5
13	(Cl + J)/2	= Br	= 40.6	17.7	40	63.5
14	(S + Te)/2	= Se	= 40.1	16	39.7	64.2
15	(P + Sb)/2	= As	= 38	16	37.5	60
16	(Ta + Ti)/2	= Sn	= 58.7	92.3	59	25
17	(W + Mo)/2	= V	= 69	92	68.5	46
18	(Pa + Rh)2	= Ru	= 52.5	53.2	52.1	51.2
19	(Os + Ir)/2	= Pt	= 98.9	99.4	99	98.5
20	(Bi + Au)/2	= Hg	= 101.2	104	100★	98.4★

★ In the original version, these two atomic weights have been inadvertently interchanged. Norium was an element that was first reported in 1845 but was not later comfirmed.

E. Lenssen, Über die Gruppierung der Elemente nach ihrem chemisch-physikalischen Charakter, *Annalen der Chemie und Pharmazie*, 103, 121–131, 1857.

Lenssen was another early pioneer who was prepared to make predictions on the basis of his system. For example, he predicted the atomic weights of erbium and terbium, neither of which had yet been isolated. This is mentioned just to emphasize again that Mendeleev did not "invent" the idea of making predictions using classification systems for the elements, as seems to be popularly believed. The fact remains, however, that Lenssen's predictions were found to be incorrect.

Many philosophical issues regarding the prediction of new elements and properties of elements are examined at various points in this book. One of these issues concerns the importance that is attributed to predictions while a theory is in the process of being accepted. This theme has been actively debated by recent historians and philosophers of science, and it has some implications for the story of the periodic table, the development of which is usually presented as relying heavily on the prediction of new elements.[73]

TABLE 2.10
Lenssen's supertriads.

Triad	*Mean equivalent weight*	
1	23	
3	33	(23 + 44)/2 = 33.5
2	44	
	28	
6	?	
5	47	
9	29.5	
8	33.5	(29.5 + 37)/2 = 33.3
7	37	
H	1	
11	7	(1 + 12)/2 = 6.5
12	12	
15	38	
14	40	(38 + 40)/2 = 38
13	40	
18	52.1	
16	61	(52.1 + 69)/2
17	69	
19	99	
20	101	(99 + 104)/2 = 101.5
10	104	

Triads are numbered as in table 2.9.

E. Lenssen, Uber die gruppirung der elemente nach ihrem chemisch-physikalischen charakter, *Annalen der Chemie und Pharmazie*, 103, 121–131, 1857.

But at the close of this chapter, it should be appreciated how far chemistry had advanced from the introduction of numerical aspects by Lavoisier and others at the time of the chemical revolution to the growing realization that such numerical aspects of chemistry were also essential to the classification of the elements. Indeed, it appears that real progress was achieved only when the debate over Prout's hypothesis and the hunt for triads served to focus attention on the role of numerical values, whereas the previous attempts to sort the elements according to chemical similarities had failed to produce any coherent scheme. And all of this occurred before it was discovered that simply ordering the elements according to increasing values of atomic weight would reveal a periodicity in their properties.

The story of the early development of the periodic table demonstrates very effectively how scientific ideas can progress in spite of what later appear to be mistakes. For example, many of the triads that were identified have turned out to be incorrect in that they made no chemical sense, and yet the general project of examining triad relationships was still rather fruitful. Local mistakes do not seem to matter too much. One might consider the case of Dalton, for example. Three of his main ideas—the importance of repulsions between like particles; the existence of a caloric, or heat envelope, around atoms; and the formula of OH he assumed for water—have all turned out to be incorrect. Nevertheless, Dalton's general project has been tremendously influential. Indeed, his atomic theory represents one of the pillars of modern science, providing a theoretical understanding of the observed laws of chemical combination, among other chemical facts. It is as if scientific evolution somehow transcends any logical stepwise progression and yet still displays a form of organic growth within which any "mistakes" are subsumed. This overall evolution seems to have a life of its own, which overrides mistakes on the part of individual scientists, or even collective errors, in the light of subsequent knowledge.[74]

Postscript on Triads

As I have shown, the recognition of triads represented the first important step toward the eventual construction of the modern periodic system. The limitations of the concept of triads had more to do with the data that were being used by the early pioneers than with the concept itself. It is interesting to consider how triads fare in the modern periodic system.

It is now realized that atomic weight is not the fundamental property determining the placement of each element in the periodic table. The elements can indeed for the most part be ordered by increasing weight, but the atomic weight of any particular element depends upon the contingencies of terrestrial abundances of all the isotopes of that particular element. When they measured the atomic weight of an element, nineteenth-century chemists were unwittingly measuring the average weight of a mixture of isotopes (except for those elements that occur as a single isotope in nature.[75]

As was discovered well after the turn of the twentieth century, when the structure of the atom was discerned, the order of the elements is determined unambiguously by the property of atomic number, which corresponds to the number of protons in the nucleus of the atoms of any particular element. It emerges that in certain parts of the modern periodic table the triad relationship turns out to be exact if atomic numbers are used instead of atomic weights (table 2.11). For example, a number of the triads discovered by Döbereiner behave in this manner.

I postpone the full explanation for why perfect triads occur in parts of the periodic system until chapter 6, where I give an account of the discovery of isotopes and atomic number. From the perspective of the modern periodic table, about 50% of all possible vertical triads, using atomic numbers, are in fact exact.

TABLE 2.11
Döbereiner's triads computed using atomic numbers.

Element	*Atomic weight*	*Mean*	*Atomic number*	*Mean*
Chlorine	35.457		17	
Bromine	79.916	81.19	35	35
Iodine	126.932		53	
Sulfur	32.064		16	
Selenium	79.2	79.78	34	34
Tellurium	127.5		52	
Calcium	40.07		20	
Strontium	87.63	88.72	38	38
Barium	157.37		56	
Phosphorus	31.027		15	
Arsenic	74.96	76.40	33	33
Antimony	121.77		51	

Compiled by the author.

Atomic Weight Determination

In this final section, I take up the question of the determination of atomic weights that was begun by Dalton at the beginning of the nineteenth century. As noted above, Dalton adopted the rule of maximum simplicity regarding formulas, but unfortunately, this rule is broken in the vast majority of compounds such as water, ammonia, and all the oxides of nitrogen apart from NO. Moreover, whereas Dalton began by using comparative densities of gases to estimate atomic weights along with the notion of equal volumes equal numbers of particles (EVEN), he later turned against this hypothesis.

The next major contributor to the project of determining atomic weights was Berzelius, who published tables of atomic weights in 1814 and 1818, which he greatly extended and revised in 1826. Among the many problems encountered by chemists working to determine atomic weights was the question of selecting a standard. Whereas Dalton had quite reasonably chosen H = 1, not all elements combine with hydrogen. To determine the atomic weight of an element that does not react directly with hydrogen required using an intermediate element, thus increasing the sources of errors.[76]

Since oxygen forms compounds with most elements, it was adopted as the standard but was confusingly given different values by different chemists.[77] Berzelius was one of the few who tried to go beyond equivalent weights in order to determine atomic weights. As mentioned above, the determination of atomic weights depended on recognizing the correct formula for a compound. Using Gay-Lussac's law of definite proportions by volumes, Berzelius arrived at the correct formulas for water, ammonia, hydrogen chloride, and hydrogen sulfide: H_2O, NH_3, HCl, and H_2S. But Gay-Lussac's law was limited to combining gases, although Berzelius devised a method for compounds such as $PbSO_4$ and also ventured to estimate the atomic weights of a number of metals by similar approaches. In his earliest tables of 1814 and 1818, Berzelius regarded metals as dioxides, giving them formulas such as AgO_2 and FeO_2. In 1826, he changed to regarding them as monoxides, thus making the values of alkali metals twice what they should have been but obtaining correct values for the alkaline earths.

Two major developments then followed that permitted better atomic weight determinations. They were the law of Pierre-Louis Dulong and Alexis-Thérèse Petit and the law of isomorphism.

Dulong and Petit discovered that the specific heat of any solid element multiplied by its atomic weight is approximately equal to a constant (table 2.12). In fact, they adjusted the atomic weights of many elements with uncertain weights so that their behavior would fit their new law. There was little justification for taking such an action except that it seemed to preserve the putative law. Although they had originally hoped to use the law in order to determine unknown atomic weights, its approximate nature meant that this was not possible. Nevertheless, the law of Dulong and Petit proved to have another important use. It could be used to check possible atomic weights and to settle cases in which there was some doubt as to whether the supposed value needed to be halved, doubled, or kept intact. For example, from Dulong and Petit's law, it quickly became clear that Berzelius's values for the alkali metals were in error by a factor of 2 and that his formulas needed adjustment to M_2O instead of MO.[78]

TABLE 2.12
Table from Dulong and Petit's article of 1819.

Element	*Speciic heat*	*Atomic weight O = 1*	*Product of atomic weight and specific heat*
Bismuth	0.0288	13.30	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.014	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0012	4.03	0.3675
Copper	0.0949	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulfur	0.1880	2.11	0.3780

As the attentive reader may note, Dulong and Petit are not consistent in quoting values in the fourth column to the correct number of significant figures.

P.L. Dulong, A.T. Petit, Recherches sur quelques points importants de la Théorie de la Chaleure, *Annales de Chimie Physique*, 10, 395-413, 1819.

In 1819, Eilhard Mitscherlich began to publish articles in Berlin on what would become a law named after him. He found that certain elements could substitute for each other to produce analogous or, as he termed them, isomorphic structures having the same crystalline form apart from some minor variations in the angles between crystal planes.[79] He suggested that the crystal form was determined uniquely by the number of atoms in the chemical compound in question. One could therefore deduce the atomic weight of one element in a compound from the known atomic weight of another element that could act as a substitute for the first element. Recall that the problem had been to assign a particular number of atoms of any particular element to a compound, such as the classic case of Dalton's HO as opposed to Berzelius's H_2O. Here was a new way of settling such questions in the case of solid crystalline compounds. For example, by considering the two isomorphous compounds of potassium sulfate (K_2SO_4) and potassium selenate (K_2SeO_4), and from the known atomic weight of sulfur, which was 32, Mitscherlich was able to deduce the correct atomic weight of selenium to be approximately 79.[80]

Another chemist who made important contributions to the determination of atomic weights was Dumas, as mentioned above, in connection with his work on triads. In 1826, he devised a new method that permitted atomic weights to be determined for any liquid or solid substance that could be vaporized.[81] The density of the vapor produced could be compared with that of hydrogen, and on the basis of the EVEN hypothesis, the atomic weight of the vaporized element could be determined. Dumas was thus one of the few chemists making use of the hypothesis of Avogadro and André Ampère. But later, Dumas found a number of clearly anomalous atomic weights for elements, including sulfur, phosphorus, and arsenic. Faced with these problems, Dumas turned against the EVEN hypothesis, believing it to be defective in the case of elements in the gaseous state. In 1836, he became even more pessimistic and now directed his criticisms against the use of atoms in chemistry. He wrote,

> What remains of the ambitious excursion we allowed ourselves into the domain of atoms? Nothing, at least nothing necessary. What remains is the conviction that chemistry lost its way, as usual when, abandoning experiment, it tried to find its way through the mists without a guide.... If I were master I would erase the word "atom" from the science, persuaded that it goes beyond experiment; and in chemistry we should never go beyond experiment.[82]

Conclusion

It is rather surprising that both Prout's hypothesis and the notion of triads are essentially correct and appeared problematic only because the early researchers were working with the wrong data. Prout was essentially correct when he asserted that the elements could be ordered in such a way that they represented whole multiples of hydrogen. It is now known that each element contains one more proton than the last as one moves across the periodic table, and this is what determines atomic number. Thus, in a sense all the elements are indeed composites of hydrogen atom, since the number of protons in any element is an exact multiple of the single proton found in the nucleus of the hydrogen atom. The problem had been that chemists had focused on trying to make atomic weights exact multiples of each other, not realizing that atomic weights included contributions from neutrons. But the numbers of neutrons vary among each isotope, thus upsetting the simple ratios expected from Prout's hypothesis. Eventually, the switch from atomic weight to atomic number would remove the inexactness that had caused chemists to abandon Prout's hypothesis as a useful tool in the classification of elements.

Similarly, the notion of triads was essentially correct but did not always work perfectly because early chemists were using the wrong data. Indeed, from the perspective of the modern table and using atomic numbers, about 50% of all possible triads are exact.

Finally, it should be borne in mind that much of this work was carried out using equivalent weights or incorrect atomic weights. It became possible to develop successful periodic systems, which would accommodate all the elements into coherent systems, only when a set of consistent atomic weight could be obtained.

Atomic weights as distinct from equivalent weights were determined starting with Dalton's researches. However, these weights depended on knowing how many atoms of a particular element were present in a compound, something that was not well understood and over which Dalton made many errors because of his assumption of maximum simplicity. Atomic weight measurements were originally restricted to gaseous elements such as oxygen or nitrogen. Soon new methods were developed by Dulong and Petit as well as Mitscherlich and Dumas, which could be applied to elements in other states of aggregation.

FIGURE 2.6
Stanislao Cannizzaro. Photo from Edgar Fahs Smith Collection by permission.

Nevertheless, much confusion still remained. For example, very few chemists accepted the EVEN hypothesis as first announced by Avogadro and Ampère. Dumas, one of the few who did, lost his nerve when he ran across elements that yielded what seemed to be highly anomalous atomic weights. The problems would be resolved only when Cannizzaro (figure 2.6) insisted on the correctness of Avogadro's hypothesis and elaborated a method that finally gave a set of correct and consistent atomic weights.[83] It is to Cannizzaro's work that we turn our attention in the next chapter.

Notes

1. The role of physics cannot be eliminated, however. John Dalton was concerned with the physics of the air in the early research that led to his atomic theory.

2. B. Bensaude-Vincent, A Founder Myth in the History of Sciences? The Lavoisier Case in L. Graham, W. Lepenies, P. Weingart (eds.), *Functions and Uses of Disciplinary Histories*, Reidel, Dordrecht, Netherlands, 1983, pp. 53–78.

3. This is not to suggest that Lavoisier was the first to use the chemical balance, as some popular accounts would have it. There is some evidence that the balance was already being used by Johann van Helmholt, one of the leading alchemists of his day. W.R. Newman, L.M. Principe, *Alchemy Tried in the Fire: Starkey, Boyle and the Fate of Helmontian Chymistry*, Chicago University Press, Chicago, 2002.

4. However, Lavoisier seems to have also regarded oxygen as a principle rather than a simple substance, thus diminishing his break with the past.

5. These aspects have been stressed by J.B. Gough, Lavoisier and the Fulfillment of the Stahlian Revolution, *Osiris*, 2nd series, 4, 15–33, 1988.

6. R. Siegfried, M.J. Dobbs, Composition, A Neglected Aspect of the Chemical Revolution· *Annals of Science*, 24, 275–293, 1968.

7. But as I describe in chapter 4, Dmitri Mendeleev would later resuscitate the notion of abstract elements, which would serve a crucial role in his periodic classification.

8. E.g., several of Lavoisier's alleged simple substances appear to be more akin to abstract elements, or principles, even by Lavoisier's own descriptions. This is true of *lumière* and *calorique*, as described in chapter 1, and even *oxygène*, *azote* (nitrogen), and *hydrogène*.

9. For a short account of atomism and its origins in Greek philosophy, see William R. Everdell's review of Bernard Pullman's book *The Atom in the History of Human Thought*, in *Foundations of Chemistry*, 1, 305–309, 1999.

10. B. Pullman, *The Atom in the History of Human Thought*, Oxford University Press, New York, 1998.

11. I. Newton, *Opticks*, Query 31, London, 1704; also see A.R. Hall, *An Introduction to Newton's Opticks*, Clarendon Press, Oxford, 1993.

12. Some authors use the term "positivist" to describe Lavoisier's philosophical approach. I will avoid this term in view of the more technical sense of the word "positivism," which followed Auguste Comte's later usage of the term.

13. As discussed in chapter 4, Mendeleev held a similar view of the existence of distinct elements, whereas his leading competitor, Julius Lothar Meyer, believed in the essential unity of matter.

14. Dalton's reasons for arriving at his atomic theory have a complicated and incomplete history. This is because many of his papers were lost in a fire during the Second World War.

15. F. Greenaway, *John Dalton and the Atom*, Heinemann, London, 1966; A.J. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State University Press, Columbus, 1984.

16. Dalton's assumption of binary formulas for water and ammonia is taken up later in this chapter.

17. This conclusion is not quite as inevitable as I imply here, however. For a different opinion, see, e.g., P. Needham, Has Daltonian Atomism Provided Chemistry with Any Explanations? *Philosophy of Science*, 71 (2004), 1038–1047. A closely related article is P. Needham, When Did Atoms Begin to Do Any Explanatory Work in Chemistry?, *International Studies in the Philosophy of Science*, 18 (2004), 199–219. Needham's view is based, in part, on that of Pierre Duhem. See Needham's translation of Duhem's article, Atomic Notation and Atomistic Hypotheses Translated by Paul Needham, *Foundations of Chemistry*, 2, 127–180, 2000; For a response to Needham, see K.R. Zwier, Dalton's Chemical Atoms versus Duhem's Chemical Equivalents, *Philosophy of Science*, 78, 842–853, 2011.

18. As mentioned in chapter 1, the notion that equivalent weights are purely empirical is problematic, although perhaps more true of Richter's early tables involving just reactions between acids and metals.

19. This statement is not quite true since two oxygen atoms can also combine with two atoms of hydrogen to form hydrogen peroxide. Fortunately, this complication did not arise in Dalton's time, since hydrogen peroxide had not yet been discovered when he began his work. The value of 8 for the atomic weight of oxygen is more in keeping with the modern value. Dalton's original estimate of the atomic weight of oxygen was 7 rather than 8 because of experimental inaccuracies. Nevertheless, he soon corrected it from 7 to 8 when better experimental data became available.

20. Dalton was well aware of the arbitrary nature of his rule of simplicity. In 1810, he discussed the possibility that water could be a compound of three atoms, two of hydrogen and one of oxygen, in which case the atomic weight of oxygen would be 14. In fact, water does consist of these three atoms, and the modern atomic weight of oxygen is closer to 16 than 14. In the same time, Dalton also discussed the possibility that water might consist of two atoms of oxygen and one of hydrogen, which would give oxygen an atomic weight of 3.5. As mentioned in note 19, Dalton originally believed that the atomic weight of oxygen was 7 rather than 8, hence explaining his estimate of 14 rather than 16 for the atomic weight of oxygen when using the correct formula for water.

21. J.F. Gay-Lussac, *Alembic Club Reprints*, No. 4, Edinburgh, reprinted 1923.

22. In modern terms, we would write the reaction as

$$2H_2 + O_2 \rightarrow 2H_2O$$

Since the right-hand side includes a substance containing a single oxygen atom, it appears that the oxygen molecule on the left side must be divisible; hence, it is written as O_2. Up to this point, today's notion of "diatomic molecules" had not been arrived at.

23. It appears that Dalton had implicitly used the EVEN hypothesis in estimating the relative weights of the atoms of different gaseous elements from their relative densities.

24. Anonymous, On the Relation between the Specific Gravities of Bodies in the Gaseous State and the Weights of Their Atoms, *Annals of Philosophy (Thomson)*, 11, 321–330, 1815.

25. Anonymous, Correction of a Mistake in the Essay on the Relation between the Specific Gravities, etc., *Annals of Philosophy (Thomson)*, 12, 111, 1816.

26. The classic historical and philosophical study on Prout is William Brock, *From Protyle to Proton*, Adam Hilger, Boston, 1985.

27. *Collected Works of Sir Humphry Davy*, edited by his brother John Davy, Smith, Elder & Co., London, 1839–1840, vol. 5, p. 163.

28. Berzelius's own values underwent many revisions in successive published versions. E.g., the following selected elements show how his later values contained many nonintegral values:

	Mg	Al	Cl	Zn
1815 value	50	55	70	128
1828 value	25.4	27.4	35.5	64.6

29. Berzelius's weights are relative to the oxygen standard, whereby O = 16.

30. J. Berzelius, Tafel über die Atomengewichte der elementaren Körper und deren hauptsächlichsten binairen Vebindungen, *Annalen der Physikalishe Chemie*, 14, 566–590, 1828.

31. L. Gmelin, *Handbuch der theoretischen Chemie*, Frankfurt, 1827, as cited on p. 23 of F.P. Venable, *The Development of the Periodic Law*, Chemical Publishing Co., Easton, PA, 1896.

32. These whole number coincidences involving carbon, oxygen, and nitrogen were not evident from the early published values of equivalent and atomic weights. Carbon initially showed values of 12.2 and 12.3, and it was not until 1843 that a value of 12 was obtained. Oxygen was assigned values of 5.5, 7, and 7.6 in various early tables. The value of 16 emerged in 1815. Finally, nitrogen appeared as 14.2 until 1843, when Charles Gerhard's table gave the value of 14.

33. J.S. Stas, Researches on the Mutual Relations of Atomic Weights, *Bulletin de l'Académie Royale de Belgique,* 10, 208–350, 1860.

34. J.S. Stas, Sur les Lois des Proportions Chimique, *Memoires Academiques de L'Académie Royale de Belgique*, 35, 24–26, 1865.

35. R.J. Strutt, On the Tendency of the Atomic Weights to Approximate to Whole Numbers, *Philosophical Magazine*, 1, 311–314, 1901.

36. Many common elements show one predominant isotope, and as a result, their atomic weights are very close to integral multiples of the weight of the hydrogen atom. Hydrogen itself consists of about 99.99% of one particular isotope. Carbon is 98.89% carbon-12, nitrogen is 99.64% nitrogen-14, oxygen is 99.76% oxygen-16, sulfur is 95.0% sulfur-32, and fluorine is 100% fluorine-19.

37. Writers on the periodic system have tended to downplay Prout's hypothesis, perhaps due to Whiggish tendencies and the fact that it has turned out to be incorrect. One exception is F.P. Venable's classic history of the early stages of the periodic system, in which he makes the following highly laudatory remark about Prout's idea: "Probably no hypothesis in chemistry has been so fruitful of excellent research as this much discussed hypothesis of Prout" (*The Development of the Periodic Law*, Chemical Publishing Co., Easton, PA, 1896, p. 3).

38. Why Döbereiner chose to begin his work with oxides is not known. These compounds had recently been isolated in England by Davy and might thus have aroused general interest. In addition, working with the oxides would not have required the isolation of the elements and would therefore present an easier experimental option.

39. It is worth emphasizing that, contrary to the accounts still found in many chemistry textbooks, Döbereiner's discovery of triads, whose middle member has approximately the mean weight of the two flanking members, did not in fact concern elements but instead their compounds.

40. These values were recalculated by Johannes van Spronsen using a correct atomic weight for oxygen of 16 instead of the value of 7.5 that Döbereiner used.

41. In fact, nuclear reactions *can* result in transmutation of elements, in a different sense, as first discovered in the twentieth century by the physicist Ernest Rutherford.

42. A printer's error was probably responsible for this small error in the calculated mean, which should be 80.97.

43. Döbereiner was working with incorrect formulas for the oxides of these elements, MO instead of M_2O, with the result that his atomic weights appear to be about twice the currently accepted values.

44. This seems to be another printer's error and more serious this time since the mean should be 84.241.

45. There is a sense in which the chemical properties can be regarded as more basic since the purpose of the exercise is to obtain a chemical classification. Numerical data serve to formalize the system and sometimes to resolve cases that may be difficult to decide on the basis of chemical properties. Nevertheless, this question of the relative importance to be attached to chemical and numerical properties is in itself an important issue that will recur in this book.

46. I am not claiming that this system is unknown to other authors, only that it has been highly neglected.

47. Rather than being literally a "hand" book, this work amounted to a massive 18 volumes.

48. Gmelin obtained a value of 20.5 for calcium by direct determination.

49. If one examines the later system of John Hall Gladstone, which is almost exclusively based on Gmelin's system under discussion, this reveals that Gmelin did in fact order most elements according to trends in their atomic weights. J.H. Gladstone, On the Relations between the Atomic Weights of Analogous Elements, *Philosophical Magazine*, 5(4), 313–320, 1853.

50. Nevertheless, Gmelin's ordering within a family of chemically similar elements is explicitly based on the earlier concept of electronegativity.

51. Whether to present chemistry inductively or deductively ultimately depends on each author's philosophical taste. It is by no means clear that Mendeleev's apparent decision to proceed inductively is the only correct option.

52. Numerous subsequent volumes have continued this detailed survey of the chemical properties of the elements.

53. This incorrect placement cannot be blamed just on Gmelin since it recurs in many later periodic systems.

54. Somewhat surprisingly, the excellent book on the early history of the periodic system written by F.P. Venable (*The Development of the Periodic Law*, Chemical Publishing Co., Easton, PA, 1896) fails to even mention Gmelin's system.

55. J. van Spronsen, *The Periodic System of the Chemical Elements, the First 100 Years*, Elsevier, Amsterdam, 1969, p. 70.

56. This is all the more puzzling given that van Spronsen even mentions this fact on the same page, although in a different context. Van Spronsen also criticizes Gmelin for not seeming to arrange the elements in order of increasing atomic weight. But Gmelin may well have based his system on atomic weights, though perhaps a little erratically. It is difficult to see how he can be said to have "demoted" atomic weight in producing his system, as van Spronsen claims.

57. Helga Hartwig (chief ed.), *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Springer-Verlag, Berlin, 1988.

58. For a detailed historical account of the evolution of the concept of electronegativity, see W.B. Jensen, Electronegativity from Avogadro to Pauling: Part 1: Origins of the Electronegativity Concept, *Journal of Chemical Education*, 73, 11–20, 1996; and Jensen, Electronegativity from Avogadro to Pauling: II. Late Nineteenth-and Early Twentieth-Century Developments, *Journal of Chemical Education*, 80, 279–287, 2003.

59. Chlorine forms acids, which Gmelin gives as ClO_3 and ClO_4 in addition to ClO_5 and ClO_7. The fact that all mineral acids contain hydrogen had not yet been realized.

60. In contemporary terms, one might also see the differences between fluorine and the other halogens as resulting from the phenomenon of first-member anomaly, whereby the

uppermost element in the main-group elements shows anomalous behavior when compared with other group members.

61. The question of the placement of tellurium takes on some importance in view of its being one of the few elements that belong to a reversed pair, the other element in this case being iodine. Many pioneers of the periodic system reversed the positions of tellurium and iodine in order to better reflect their respective chemical analogies. It would appear that this was more easily decided for iodine than for tellurium, given Gmelin's apparent uncertainty in the chemical analogies of tellurium.

62. The omission of nitrogen from the group that includes phosphorus, arsenic, and antimony may be because nitrogen alone occurs as a gas, while the other three elements mentioned are all solids at room temperature. In addition, the properties of nitrogen are somewhat anomalous, in keeping with the phenomenon of first-member anomalies, once again from the perspective of contemporary knowledge. Similarly, Gmelin did not include oxygen, a gas at room temperature, with sulfur and selenium, two solids with which it is grouped in the modern periodic table.

63. The other elements that would eventually join this trio of elements are rubidium and cesium, discovered in 1860 and 1861, respectively.

64. Gmelin places beryllium in a neighboring group along with cerium and lanthanum. This would be regarded as a mistake from the perspective of the modern table, in which beryllium is a group II main-group element while the other two are rare earths. Radium had not yet been discovered.

65. As noted above, Gmelin had discovered that magnesium, calcium, and barium form a triad.

66. Formulas given by Gmelin for the oxides were LiO, NaO, CaO, and BaO. In modern terms, only the third and fourth of these are correct. The first two should read Li_2O and Na_2O, respectively.

67. For some interesting remarks on the nature of prediction and its relationship to scientific laws as seen by Mendeleev, see M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004.

68. This lecture was subsequently published in the scientific journals of various European countries and thus exerted considerable influence on chemists worldwide.

69. Michael Faraday, *A Course of Six Lectures on the Non-metallic Elements. Before the Royal Institution*, Royal Institution, London, 1852.

70. Of course, *some* of these elements do have things in common, namely, O, S, and Se, all of which are grouped together in group 16 of the modern periodic table.

71. The subject of secondary relationships is taken up in chapter 10. This feature is revealed in the older short-form tables as well as pyramidal displays of the periodic system but not, unfortunately, in the currently popular medium-long form.

72. E. Lenssen, Uber die gruppirung der elemente nach ihrem chemisch-physikalischen charackter, *Annalen der Chemie Justus Liebig*, 103, 121–131, 1857.

73. Many articles have appeared on this issue, including S.J. Brush, The Reception of Mendeleev's Periodic Law in America and Britain, *Isis*, 87, 595–628, 1996; R. Campbell, T. Vinci, Novel Confirmation, *British Journal for the Philosophy of Science*, 34, 315–341, 1983; P. Maher, Prediction, Accommodation and the Logic of Discovery, in A. Fine, J. Leplin (eds.), *PSA 1988*, vol. 1, Philosophy of Science Association, East Lansing, MI, 1988, 273–285; J. Worrall Fresnel, Poisson and the White Spot: The Role of Successful Prediction in the Acceptance of Scientific Theories, in D. Gooding, T. Pinch, S. Schaffer (eds.): *The Uses of Experiment*, Cambridge University Press, Cambridge, 1989, pp. 135–157; E.R. Scerri, J. Worrall, Prediction and the Periodic Table, *Studies in History and Philosophy of Science*, 32, 407–452, 2001.

74. This could be regarded as a form of nonrational development in science, but not in the sense implied by Thomas Kuhn, for whom rival scientific theories cannot be strictly compared because they speak different languages such that translation is never quite possible.

75. There are 21 elements that show just one single isotope. They include sodium, cesium, beryllium, aluminum, phosphorus, arsenic, bismuth, fluorine, iodine, manganese, cobalt, and gold. Also see note 36. (Throughout this book I use the American spelling for the elements whose symbols are Al and Cs rather than the official IUPAC spelling of aluminium and caesium.)

76. In addition, hydrides did not lend themselves to very accurate analysis. E.g., for several years water was reported to contain 13.27% hydrogen until Pierre Dulong corrected this measurement to 11.1%.

77. The following four chemists used four different values: Thomas Thomson, 1; William Wollaston, 10; Berzelius, 100; Stas, 16. The final value most closely approximates the modern value and is consistent with an approximate value of 1 for hydrogen.

78. The law of Dulong and Petit failed for a number of elements such as carbon, silicon, and boron due to variations in their specific heats with increasing temperature. This issue is taken up again in chapter 5.

79. S. Mauskopf, Crystals and Compounds: Molecular Structure in Nineteenth Century French Science, *Transactions of the American Philosophical Society*, 66, 3, 5–82, 1976.

80. Dalton had incorrectly assigned an atomic weight of 40 to selenium, while Berzelius and others did not venture any value whatsoever in their early tables of atomic weights. In 1927, Berzelius adopted Mitscherlich's value, which he cited as 79.1.

81. J.B.A. Dumas, Memoire sur Quelques Points de la Theorie Atomique, *Annales de Chimie et Physique*, 33(2), 334–414, 1826.

82. J.B.A. Dumas, *Leçons sur la philosophie chimique*, 1837, reprint in Editions Culture et Civilization, Brussels (1972), p. 249.

83. The problem with the anomalous elements was solved by Marc Antoine Gaudin, who suggested that molecules of different elements might contain different numbers of atoms. E.g., sulfur would be hexa-atomic, while mercury was monoatomic. M.A.A. Gaudin, Recherches sur la structure intime des corps inorganiques, *Annales de Chimie et Physique*, 52(2) 113–133, 1833. A discussion of a more recent method of determining atomicity using the kinetic theory is given in chapter 5 in connection with the noble gases.

CHAPTER
3

DISCOVERERS OF THE PERIODIC SYSTEM

The periodic system was not discovered by Dmitri Mendeleev alone, as is commonly thought, or even just by Mendeleev and Julius Lothar Meyer. It was discovered by as many as five or six individuals at about the same time, in the decade of the 1860s, following the rationalization of atomic weights at the Karlsruhe conference.[1]

It became apparent by the middle of the nineteenth century that something needed to be done to resolve the widespread confusion over equivalent and atomic weights. Amedeo Avogadro had already proposed a solution to Gay-Lussac's law that preserved John Dalton's indivisible elemental particles. Recall that Gay-Lussac had observed that volumes of gases entering into chemical combination and their gaseous products are in a ratio of small integers. Dalton had refused to accept this viewpoint because it implied that atoms appeared to divide in some instances, such as the combination of hydrogen and oxygen to create steam. Avogadro had suggested that such "atoms" must be diatomic; that is, in their most elemental form they must be double. Thus, the oxygen atom was not dividing; rather, it was an oxygen molecule, which consisted of two oxygen atoms, that was coming apart.

Unfortunately, the terms in which Avogadro expressed his views were rather obscure and failed to make much impression on the chemists of the day. Two exceptions were the French physicist and chemist André Ampère[2] and the Alsatian chemist Charles Gerhardt,[3] both of whom adopted the view that elemental gases were composed of diatomic molecules.

One consequence of the general refusal to recognize the existence of diatomic molecules as the ultimate "atoms" of gaseous elements was that, as mentioned in chapter 2, the confusion between equivalent weights and atomic weights continued to reign. Although the relative weights of oxygen to hydrogen in water are approximately 8 to 1, the relative weight of the oxygen atom to the hydrogen atom takes on values of 8 or 16 depending on what one considers the correct formula for water to be. Dalton opted for a formula of HO for water, which meant that he was forced to assume an atomic weight of 8 for oxygen. Dalton allowed his insistence on the indivisibility of atoms to obscure the possibility that in some substances the smallest atom, in the chemical sense, consisted of two atoms combined together. Since this unit is still the smallest possible unit of the element in question, Dalton need not have been concerned.

But although Avogadro had proposed the solution as early as 1811, its acceptance would have to wait until 1860, by which time great confusion had developed among different chemists regarding the atomic weights of many elements and, consequently, the formulas of many compounds. The rapid growth of organic chemistry during this period and the proliferation of varying formulas for the same compounds added to the need to find a solution. When the chemist August Kekulé prepared a textbook of chemistry in the early 1860s, he listed as many as 19 different formulas for acetic acid, all of which had been used in the literature.

It was against this background that the Karlsruhe conference was convened. Its aims were to clarify the notions of "atom" and "molecule" and the related issues of equivalent weight and atomic weight. It fell to Stanislao Cannizzaro to resuscitate the work of his countryman Avogadro and to make it more palatable to the chemists who attended the conference. No new science was required, just a careful analysis of the problems at hand and a desire to bring order to the chaos surrounding the conflicting use of different atomic weights and the consequent different formulas. Once the notion that elemental gases consisted of diatomic molecules was accepted, the whole substructure of chemistry was corrected. At last, chemists interested in classifying the elements had a firm foundation on which they could build with confidence.[4]

Cannizzaro accepted Avogadro's hypothesis, namely, that equal volumes of all gases, at the same temperature and pressure, contain the same number of particles.[5] As a result, he argued that the relative density of a gas would provide a measure of its relative mass. This much was not new and had been assumed by others. What Cannizzaro did was to pursue Avogadro's hypothesis in a comprehensive manner in such a way as to finally usher in the acceptance of the hypothesis and to break the deadlock over the measurement of atomic weights. He began with the elementary assumption that if the molecular mass of hydrogen were M and if that of an element is found to be N times that of hydrogen, then the molecular mass of the unknown element would be NM. But the aim is to obtain the atomic mass (a) of any element A. Cannizzaro recognized that one could analyze a large number of compounds of the element. If it turned out, as it always did, that all the intramolecular masses of A were whole number multiples of 1 and the same mass, then that mass had the right to be called the atomic weight of A.[6]

For example, in the case of carbon, Cannizzaro published a table, on which table 3.1 is based, and proceeded to lend his full support to the idea of regarding atoms realistically:

Table 3.1
Cannizzaro's method applied to finding the atomic weight of carbon.

Species	*Mass of carbon within molecule of the species*
Carbonic acid	12
Carbonic oxide	12
Sulfide of carbon	12
Marsh gas	12
Ethylene	24
Propylene	36
Ether	48

The highest common factor of 12 from the column on the right, on this evidence, is the atomic weight of carbon.

Based on S. Cannizzaro, Sketch of a Course of Chemical Philosophy, *Il Nuovo Cimento*, 7, 321–366, 1858, Table from p. 335, translated in Alembic Club Reprints No. 18, Alembic Club Publications, Edinburgh, 1910.

> Compare, I say...the various quantities of the same element contained in the molecule of the free substance and in those of all its different compounds, and you will not be able to escape the following law: The different quantities of the same element contained in different molecules are all whole multiples of one and the same quantity, which always being entire, has the right to be called an atom....[7]

Another Brief Interlude on Qualitative Chemistry

Let us consider another textbook, written in 1867 by the French chemist Alfred Naquet, to see how much was known about the chemistry of the elements at the time when the mature periodic system was being discovered. Table 3.2, of families of the elements, has been constructed on the basis of the groups, or families, listed by Naquet.[8]

Several improvements can be seen when this table is compared with the grouping by Leopold Gmelin given in chapter 2. Naquet's 2° *famille* (family) shows that oxygen has now been correctly included among elements such as sulfur and selenium. In addition, Naquet correctly includes nitrogen among the group containing phosphorus, arsenic, and antimony and also adds bismuth.[9] Whereas Gmelin had grouped only carbon and silicon together in his own system, Naquet includes tin, in addition to three transition metals.[10] The final improvement is seen in Naquet's 1° family of metals, in which he has included the newly discovered rubidium and cesium. Different textbook authors of this period listed similar families of elements, and this kind of information would have been available to all discoverers of the periodic system, at least in principle. It is in relation to such qualitatively based systems that one must consider the discovery of the quantitatively based periodic systems that follow.

TABLE 3.2
Families of elements according to Naquet's textbook of 1867.

Metalloids

1° famille	*2° famille*	*3° famille*	*4° famille*	*5° famille*
Cl	O	B	Si	N
Br	S		C	P
I	Se		Sn	As
H	Te		Zr	Sb
			Ti	Bi
				U

Metals

1° famille	*2° famille*	*3° famille*	*4° famille*	*5° famille*	*6° famille*
K	Ca	Au	Al		Mo
Na	Sr		Mn		W
Li	Ba		Fe		Ir
Rb	Mg		Cr		Rh
Cs	Zn		Co		Ru
Ag	Cd		No		
	Cu		Pb		
	Hg		Pt		

Based on A. Naquet, *Principes de Chimie*, F. Savy, Paris, 1867. Compiled by the author.

The Rapid Appearance of Several Periodic Systems

What permitted the rapid progress toward the development of the periodic system in several different countries during the 1860s was the publication, between 1858 and 1860, of a set of consistent atomic weights by Cannizzaro, based on the above method, which he compiled in preparation for the Karlsruhe conference. Once Cannizzaro had clearly established the distinction between molecular and atomic weights, the relative weights of the known elements could be compared in a reliable manner, although a number of these values were still incorrect and would be corrected only by the discoverers of the periodic system.

Despite the pivotal role played by the rationalization of atomic weights in preparing the way for the successful sorting of the elements, it is debatable whether the fairly rapid and independent discovery of the mature periodic system over the following decade represented a scientific revolution in the Kuhnian sense. Indeed, as remarked in the introduction, the history of the periodic system appears to be the supreme counterexample to Thomas Kuhn's thesis, whereby scientific developments proceed in a sudden, revolutionary fashion. The more one examines the development of the periodic system, the more one sees continuity rather than sudden breaks in understanding. Looking at the events leading up to the introduction of Mendeleev's periodic system in 1869, we can see the concept of periodicity as evolving in distinct stages through the work of other chemists. Thus, rather than six actual discoveries of the system, it may be more correct to see it as an evolution through several systems, discovered within a period of less than 10 years.[11] The final one of these systems was by Mendeleev, who also worked harder than anyone else to establish the validity of the fully mature system. There are good reasons for singling out Mendeleev (and Lothar Meyer) in this story, and there are further grounds for making Mendeleev the one leading discoverer of the periodic system. But as I argue in this chapter, the *idea* of periodicity, which is central to the periodic system, did not originate with Mendeleev.

Other factors hastened the sudden explosion of periodic systems published in the 1860s. One of these factors was the discovery of new elements as a result of the development of the novel technique of spectroscopy. Having more elements to work with meant that there would be fewer gaps among them, making periodicity easier to discern. And spectroscopy itself, which permitted the characterization of each element by its unique spectral fingerprint, would in turn allow much greater understanding of the chemical nature of the elements.

Another important change that occurred around this time and helped to make the discovery of the periodic system possible was the increased questioning of William Prout's hypothesis (all elements are composites of hydrogen), which had figured rather prominently in the previous wave of discoveries leading up to the periodic system. In fact, such was the decline in support for Prout's hypothesis in the 1860s that chemists who still harbored such thoughts felt compelled to conceal their names. This was the case with one "Studiosus" who published an article in 1864, in response to John Newlands's periodic system, claiming that the atomic weights of the elements were multiples of 8. Meanwhile, another pro-Proutian author, who called himself "Inquirer," attempted to mediate the controversy that ensued between Newlands and Studiosus.[12]

With the decline of the Prout hypothesis, chemists became less concerned with finding neat, integral relationships among the elements. At the same time, other kinds of numerical regularities that had held the fascination of noted chemists, such as Jean-Baptiste André Dumas and Max Pettenkofer, also began to subside. While the craze for searching for numerical regularities started to fade away, the work of chemists began to show a different aim and method. Instead of trying to find isolated triads or unconnected groups, researchers were now free to focus on seeking an integrated system that would include all the known elements in a meaningful way.

In examining the work of the six discoverers of the periodic system, it is important to consider their published articles in some detail. In trying to portray an overall picture of the evolution of the periodic system, I do not concentrate exclusively on the final published tables given by these authors. In the case of Newlands and William Odling, as well as some of the others, I examine several subsidiary tables, sometimes dealing with specific comparisons between the elements. This approach reveals important aspects in the evolution of their ideas that are missed by concentrating only on the finished work of any of the discoverers.

Alexandre Émile Béguyer De Chancourtois

There are valid reasons for declaring that the periodic system was essentially discovered in 1862 by Alexandre De Chancourtois, a French geologist. De Chancourtois appears to have taken not just an important step in the story of the periodic system but, in many ways, the single most important step. It was he who first recognized that the properties of the elements are a periodic function of their atomic weights, a full seven years before Mendeleev arrived at the same conclusion.

Although he hit upon this crucial notion underlying the entire edifice of the periodic system, De Chancourtois is not generally accorded very much credit, partly because his publication did not appear in a chemistry journal and because he did not develop his insight any further over subsequent years. Indeed, it was only about 30 years after his paper appeared that De Chancourtois's claim to priority came to light through the efforts of Philip Hartog in England and Paul-Émile Lecoq De Boisbaudran as well as Albert Auguste De Lapparent in France.[13]

De Chancourtois became professor of subterranean topography at the Ecole de Mines in Paris in 1848 and then in 1856 assumed a professorship in geology at the same institution. He attempted to systematize many different areas, including knowledge of minerals, geology, and geography, and even produced a form of universal alphabet. De Chancourtois presented his system of the chemical elements to the Académie des Sciences and also published it in its journal, the *Comptes Rendus*.[14] He proposed a three-dimensional representation of the periodicity of properties as a function of atomic weight (figure 3.1). De Chancourtois used equivalent weights for the elements, although he divided many values by 2, as a result of which most of his values agreed approximately with the new atomic weights of Cannizzaro. De Chancourtois also consistently rounded off the weights to produce whole number values. Although he did not commit himself specifically to the Proutian idea of atoms being composites of hydrogen, De Chancourtois did express his support for what he called "Prout's law," whereby the values for all elements should be whole number multiples of the value for the element hydrogen.

In 1862, De Chancourtois arranged the elements according to what he termed increasing "numbers" along a spiral. These numbers were written along a line that served to generate a vertical cylinder. The circular base of the cylinder was divided into 16 equal parts. The helix was traced at an angle of 45° to its vertical axis, and its screw thread was similarly divided, at each of its turns, into 16 portions. Thus, the seventeenth point along the thread was directly above the first, the eighteenth above the second, and so on. As a result of this representation, elements whose characteristic numbers differed by 16 units were aligned in vertical columns.

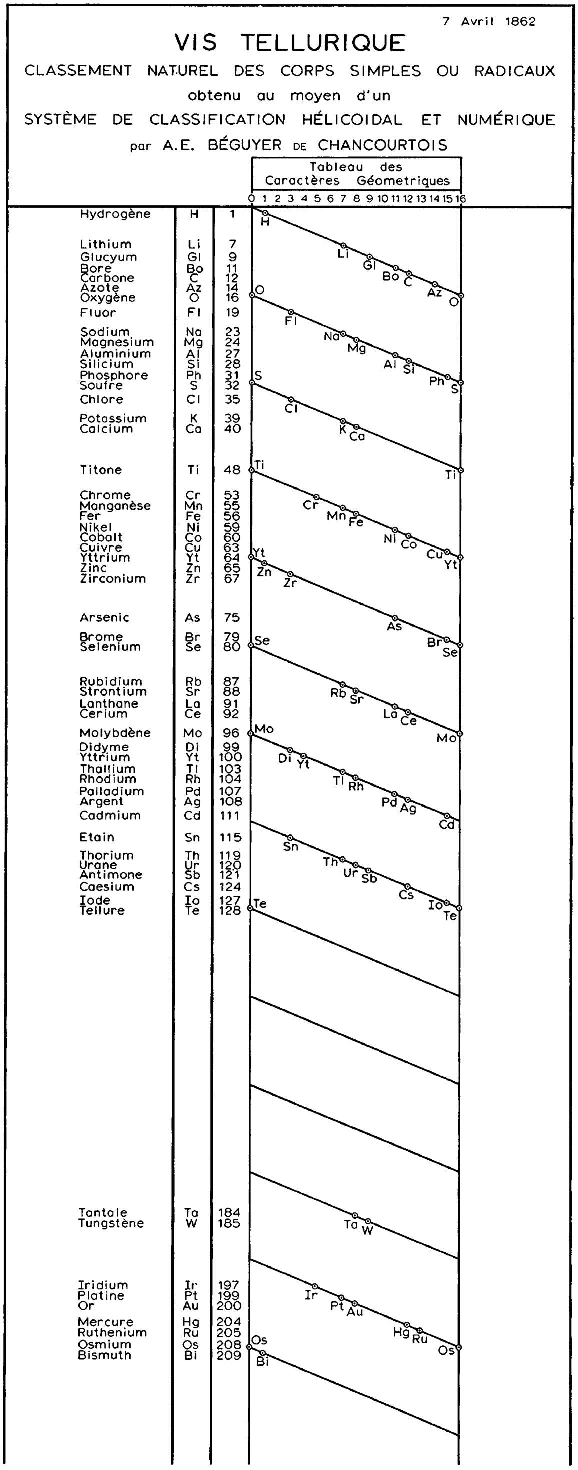


FIGURE 3.1
Telluric Screw of 1862. A.E. Béguyer De Chancourtois, Vis Tellurique: Classement naturel des corps simples ou radicaux, obtenu au moyen d'un système de classification hélicoïdale et numérique, *Comptes Rendus de L'Academie*, 54, 757–761, 840–843, 967–971, 1862. Redrawn by J. van Spronsen, *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969, p. 99. Reproduced by permission of Elsevier.

Sodium, for example, with a weight of 23, appeared one complete turn above lithium, whose value was taken as 7. The next column contained the elements magnesium, calcium, iron, strontium, uranium, and barium. One may begin to see the modern alkaline earth group emerging, the only difference being that several transition elements have also been included along the same vertical alignment. But this feature is not surprising since De Chancourtois's table is a short-form table that does not separate main-group elements from transition metals.

The first full turn of the spiral ended with the element oxygen, and the second full turn was completed at sulfur. Periodic relationships, or chemical groupings, could be seen in De Chancourtois's system, although only approximately, by moving vertically downward along the surface of the cylinder. The eighth such turn, and coincidentally the halfway point down the cylinder, occurred at tellurium. This rather arbitrary feature provided De Chancourtois with the name of *vis tellurique,* or telluric screw, for his system. This name may also have been chosen by De Chancourtois from *tellos*, Greek for earth, given that as a geologist, he was primarily interested in classifying the elements of the earth.

De Chancourtois's system did not create much impression on chemists for a number of reasons. The original published article failed to include a diagram, mainly because of the complexity faced by the publisher in trying to reproduce it, with the result that its visual force was lost. Another problem was that the system did not convey chemical similarities convincingly, as a result of the style of representation (the spiral) adopted by its author. While some of the intended chemical groupings, such as the alkali metals, the alkaline earths, and the halogens, did indeed fall into vertical columns, many others did not, thus making it a less successful system than it might have been. Yet another drawback to the system was the inclusion of radicals such as NH_4^+ and CH_3, as well as such compounds as cyanogen, some oxides and acids, and even some alloys.

Frustrated that the journal *Comptes Rendus* failed to include a diagram, De Chancourtois had his system republished in 1863. Because it was published privately, however, this further article received even less notice from other scientists than did the original one.[15] Still, it cannot be denied that De Chancourtois was the first to show that the properties of the elements are a periodic function of their atomic weights, or as he said himself, "*Les proprietées des corps sont les proprietées des nombres*. [The properties of bodies are the properties of numbers]."[16]

De Chancourtois intended the term "numbers" to mean the values of atomic weights, but even the improved atomic weights did not always yield clean intervals among the elements or line them up in what would appear to be the right order. However, following the eventual discovery of atomic numbers, De Chancourtois turned out to be even more correct than he might have himself imagined, as the properties of the elements are indeed a periodic function of their atomic numbers. De Chancourtois was also inadvertently prophetic in that he used whole number atomic weights, thus in effect creating an ordinal series of elements. To regard this as an anticipation of atomic number is not altogether implausible, although unlike Newlands (described below), De Chancourtois did not have a complete sequence of whole numbers in his system.

De Chancourtois's system was later criticized by Mendeleev, who in his Faraday lecture rather unfairly stated that De Chancourtois himself had not regarded his work as being a "natural system" of the elements. This lecture, given in London in 1889, seems to have provoked the English chemist Hartog, who had studied extensively in France, into making a belated priority claim on behalf of De Chancourtois. A couple of years later, De Chancourtois's cause was taken up by the French chemists Paul-Émile Lecoq De Boisbaudran and Albert Auguste De Lapparent, who attempted to make their fellow Frenchmen more aware of the neglected work on the telluric screw.

It is also interesting to note another remark De Chancourtois made in his article:

> Will not my series, for instance, essentially chromatic as they are, be a guide in researches on the spectrum? Will not the relations of the different rays of the spectrum prove to be derived directly from the law of numerical characteristics, or vice versa?[17]

The periodic table did indeed turn out to be a very powerful guide to the study of atomic spectra, and vice versa, as shown in later chapters where the influence of quantum theory is considered. In many instances, the periodic system reveals periodicity in physical as well as chemical properties. The way in which spectral lines are split by a magnetic field, for example, be it into doublets, triplets, or quartets, is something that shows periodicity, just as do chemical properties such as reactivities toward particular elements.

One final comment should perhaps be made about De Chancourtois. His lack of chemical knowledge may have been a hindrance in some cases, and conversely, his emphasis on geological factors may have misled him in the development of the periodic system. For example, he stated that the isomorphism between feldspars and pyroxenes had been the starting point of his system. The element aluminum appears to function analogously to the alkali metals, a fact that does not necessarily indicate that aluminum should be grouped together with alkali metals such as sodium and potassium. But this is precisely what De Chancourtois did in his system. In fact, he even changed the atomic weight, or characteristic weight, as he termed it, in the case of aluminum to make it fall neatly into line with the alkali metals. Had he known more chemistry, he might not have taken this unjustified step.

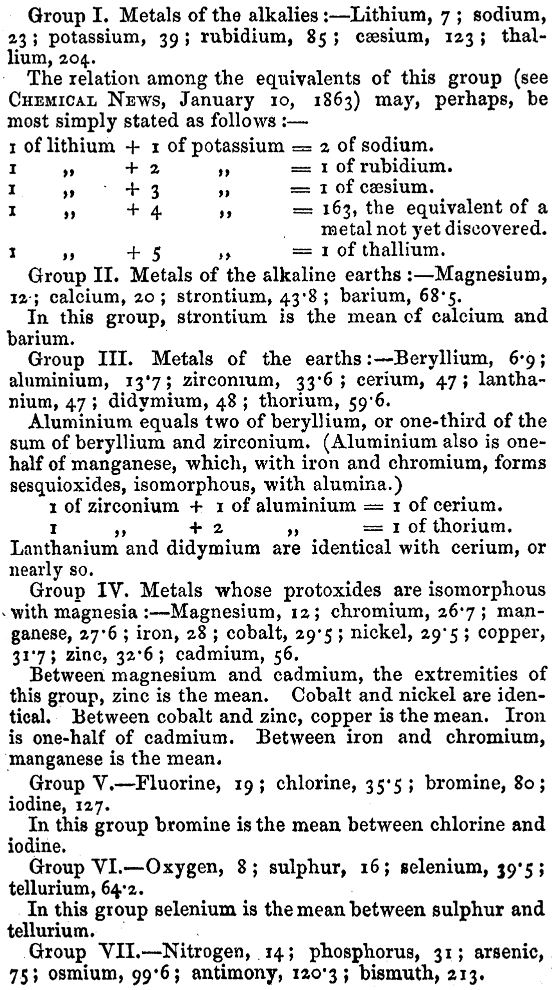
John Newlands

John Newlands was born in 1837 in Southwark, a suburb of London, which by a coincidence was also the birthplace of William Odling, another pioneer of the periodic system. After studying at the Royal College of Chemistry in London, Newlands became the assistant to the chief chemist of the Royal Agricultural Society of Great Britain. In 1860, he served briefly as an army volunteer with Giuseppe Garibaldi, who was fighting the revolutionary war in Italy. The reason for Newlands's sortie seems to have been connected to the fact that his mother was of Italian descent. It also meant that Newlands was not able to attend the Karlsruhe conference of the same year, although since he was not a major chemist at the time he would probably not have been invited. After returning to London, Newlands began working as a sugar chemist, while also supplementing his income by teaching chemistry privately, but he was never to hold an academic position.

Newlands's first attempt at classification concerned a system for organic compounds that he published in 1862 along with proposals for a new system of nomenclature.[18] In the following year, he published the first of what would be many classification systems for the elements. Although the year was 1863, Newlands developed his first system without the benefit of the atomic weight values that had been issued following the Karlsruhe conference of 1860, as he was unaware of them. Nevertheless, he did use the atomic weight values favored by Charles Gerhardt, who had begun to revise atomic weights even before the Karlsruhe conference. Thus, Newlands was able to produce a table consisting of 11 groups of elements with analogous properties whose weights differed by a factor of 8 or some multiple of 8. Because it was unfashionably Proutian, Newlands published his first article on classification of the elements anonymously, although he revealed his identity soon afterward in response to criticisms by the equally anonymous "Studiosus" (figure 3.2).

Newlands's grouping of elements in 1863 is surprisingly suggestive, especially bearing in mind that it utilizes pre-Karlsruhe atomic weights. Ever since Prout, investigators had struggled with the fact that arithmetic intervals in atomic weights among the elements are not as exact or as regular as it seems they should be. The fact that atomic weights depend upon the vagaries of isotopic mixtures for any particular element was not, of course, suspected at the time. In addition to the isotope issue, the atomic weights of many elements had not been correctly determined. Nevertheless, one cannot fail to be struck by the good fortune that Newlands and the other pioneers of the periodic system experienced in that the ordering of the elements according to atomic weight, despite their irregular intervals, corresponds almost exactly to that based on atomic number. It is almost as though nature's mixtures of isotopes had conspired together to announce the ordering that would later be discovered in terms of atomic numbers.

In his 1863 article, Newlands described a relationship among atomic weights of the alkali metals and used it to predict the existence of a new element of weight 163, as well as a new element that would be placed between iridium and rhodium. Unfortunately for Newlands, neither of these elements ever materialized. However, as has recently been pointed out, Mendeleev also made similar predictions that



Group I. Metals of the alkalies:—Lithium, 7; sodium, 23; potassium, 39; rubidium, 85; cæsium, 123; thallium, 204.

The relation among the equivalents of this group (see Chemical News, January 10, 1863) may, perhaps, be most simply stated as follows:—

1 of lithium + 1 of potassium = 2 of sodium.
1 ,, + 2 ,, = 1 of rubidium.
1 ,, + 3 ,, = 1 of cæsium.
1 ,, + 4 ,, = 163, the equivalent of a metal not yet discovered.
1 ,, + 5 ,, = 1 of thallium.

Group II. Metals of the alkaline earths:—Magnesium, 12; calcium, 20; strontium, 43·8; barium, 68·5.

In this group, strontium is the mean of calcium and barium.

Group III. Metals of the earths:—Beryllium, 6·9; aluminium, 13·7; zirconium, 33·6; cerium, 47; lanthanium, 47; didymium, 48; thorium, 59·6.

Aluminium equals two of beryllium, or one-third of the sum of beryllium and zirconium. (Aluminium also is one-half of manganese, which, with iron and chromium, forms sesquioxides, isomorphous, with alumina.)

1 of zirconium + 1 of aluminium = 1 of cerium.
1 ,, + 2 ,, = 1 of thorium.

Lanthanium and didymium are identical with cerium, or nearly so.

Group IV. Metals whose protoxides are isomorphous with magnesia:—Magnesium, 12; chromium, 26·7; manganese, 27·6; iron, 28; cobalt, 29·5; nickel, 29·5; copper, 31·7; zinc, 32·6; cadmium, 56.

Between magnesium and cadmium, the extremities of this group, zinc is the mean. Cobalt and nickel are identical. Between cobalt and zinc, copper is the mean. Iron is one-half of cadmium. Between iron and chromium, manganese is the mean.

Group V.—Fluorine, 19; chlorine, 35·5; bromine, 80; iodine, 127.

In this group bromine is the mean between chlorine and iodine.

Group VI.—Oxygen, 8; sulphur, 16; selenium, 39·5; tellurium, 64·2.

In this group selenium is the mean between sulphur and tellurium.

Group VII.—Nitrogen, 14; phosphorus, 31; arsenic, 75; osmium, 99·6; antimony, 120·3; bismuth, 213.

FIGURE 3.2
Newlands's groups of elements. J.A.R. Newlands, On Relations Among the Equivalents, *Chemical News*, 7, 70–72, 1863. Table from p. 71.

failed to materialize among elements with high atomic weights.[19] These failures can be attributed to the existence of the lanthanide elements, which occur between the second and third transition series of elements in modern terms. The lanthanides would be a problem for all the discoverers of the periodic system, as only 6 of the 14 lanthanides had been discovered prior to the 1860s, when these early periodic systems were being developed.[20]

In 1864, Newlands published his second article on the classification of the elements (table 3.3, figure 3.3). This time he drew on the more correct, post-Karlsruhe atomic weights, a version of which had been published in England by Alexander Williamson. Newlands now found a difference of 16, or very close to this value, instead of 8, between the weights of six sets of first and second members among groups of similar elements. Again, this finding seems unexpectedly accurate given that he was working with atomic weights and not atomic numbers. A very similar table comparing differences in atomic weights between first and second members of groups of analogous elements was discovered independently and published in the very same year by Odling (described below). Indeed, Odling outdid Newlands in recognizing 10 such relationships, to Newlands's six. This fact has not been given any exposure in histories of the periodic system, which sometimes fail to even mention Odling as one of the discoverers.

Less than a month after his second system appeared in 1864, Newlands published a third system that same year (figure 3.4), but in this table he included fewer elements (24, plus a space for a new element) and made no mention of atomic weights. The article is nevertheless of considerable merit since Newlands assigned an ordinal number to each of the elements, thus in a sense anticipating the modern notion of atomic number. Abandoning the arithmetic progressions in atomic weights that had bedeviled earlier investigators, Newlands simply lined the elements up in order of increasing atomic weight without concern for the values of those weights. Nevertheless, any anticipation of the modern concept of atomic weight is marred by the several cases where the sequence of elements does not strictly follow Newlands's ordinal numbers. The modern ordering based on atomic number does not show any such exceptions.

The most important thing Newland did in his third publication on the classification of the elements was to present a periodic *system*; that is, he revealed a pattern of repetition in the properties of the elements after certain regular intervals. This, of course, is the essence of the periodic law, and Newlands deserves credit for having recognized this fact so early, along with De Chancourtois. Another innovation of Newlands's later system of 1864 (which is almost universally attributed to Mendeleev, although it was also carried out by Odling) was the way in which Newlands reversed the positions of the elements iodine and tellurium in order to

TABLE 3.3
Newlands's first table of 1864.

Member of a group having lowest equivalent		*One element immediately above the preceding one*		*Difference* $H = 1$	$O = 16$
Magnesium	24	Calcium	40	16	1
Oxygen	16	Sulphur	32	16	1
Lithium	7	Sodium	23	16	1
Carbon	12	Silicon	28	16	1
Fluorine	19	Chlorine	35.5	16.5	1.031
Nitrogen	14	Phosphorus	31	17	1.062

Remade from J.A.R. Newlands, Relations Between Equivalents, *Chemical News*, 10, 59–60, 1864, table on p. 59.

				Triad			
				Lowest Term	Mean	Highest Term	
I.			Li 7	+17 = Mg 24	Zn 65	Cd 112	
II.			B 11				Au 196
III.			C 12	+16 = Si 28		Sn 118	
IV.			N 14	+17 = P 31	As 75	Sb 122	+88 = Bi 210
V.			O 16	+16 = S 32	Se 79.5	Te 129	+70 = Os 199
VI.			F 19	+16.5 = Cl 35.5	Er 80	I 127	
VII.	Li 7	+16 =	Na 23	+16 = K 39	Rb 85	Cs 133	+70 = Tl 203
VIII.	Li 7	+17 =	Mg 24	+16 = Ca 40	Sr 87.5	Ba 137	+70 = Pb 207
IX.				Mo 96	V 137	W 184	
X.				Pd 106.5		Pt 197	

FIGURE 3.3 System of 1864: J.A.R. Newlands, Relations Between Equivalents, *Chemical News*, 10, 59–60, 1864,p. 59.

		No.		No.		No.		No.		No.
Group *a*	N	6	P	13	As	26	Sb	40	Bi	54
„ *b*	O	7	S	14	Se	27	Te	42	Os	50
„ *c*	Fl	8	Cl	15	Br	28	I	41	—	—
„ *d*	Na	9	K	16	Rb	29	Cs	43	Tl	52
„ *e*	Mg	10	Ca	17	Sr	30	Ba	44	Pb	53

FIGURE 3.4 Newlands's later system of 1864. J.A.R. Newlands, On Relations Among Equivalents, *Chemical News*, 10, 94–95, 1864, p. 94.

give precedence to chemical properties over the apparent atomic weight ordering.[21] Newlands thus holds the distinction of having been the first of these three discoverers to make a so-called pair reversal.[22] It is somewhat surprising, however, especially given his emphasis on chemical properties, that Newlands failed to display analogies between several other obviously related elements, such as lithium and sodium.[23]

The Law of Octaves

In 1865, Newlands developed yet another system, which was a vast improvement on that of the previous year in that he now included 65 elements, in increasing order of atomic weight, while once again using ordinal numbers rather than actual values of atomic weight. This system was built upon his famous "law of octaves," whereby the elements showed a repetition in their chemical properties after intervals of eight elements.[24] Newlands went so far as to draw an analogy between a period of elements and a musical octave, in which the tones display a repetition involving an interval of eight notes (counting from one note of C, e.g., to the next note C inclusive). In the words of Newlands himself:

> If the elements are arranged in the order of their equivalents with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. . . . The eighth element starting from a given one is a kind of repetition of the first. This particular relationship I propose to term the *Law of Octaves*.[25]

This statement marks a rather important step in the evolution of the periodic system since it represents the first clear announcement of a new law of nature relating to the repetition of the properties of the elements after certain intervals in their sequence. As mentioned before, the periodic *law*, though not a fashionable term nowadays, is perhaps the most important aspect of the periodic table. The periodic table in all its many forms is, after all, just an attempt to represent this law graphically.

There remains the question raised earlier as to whether De Chancourtois might have been the first to recognize the existence of the periodic law. As Wendell Taylor has suggested, Newlands was far more explicit about the existence of a periodic law than was De Chancourtois, who merely mentioned it as a possibility.[26] There is little doubt that Odling also failed to recognize the existence of a fundamental law, though he did recognize the existence of a periodic system. Odling specifically claimed that, after a detailed examination of the numerical differences between the atomic weights of analogous elements, he had decided that these relations were "too numerous to depend upon some hitherto unrecognized law."[27]

Returning to Newlands's system of 1865, we note that even though it is a genuine *periodic* system, compared with his earlier lists or groups of elements, Newlands did not see the need to separate the elements into subgroups as Mendeleev later did by offsetting certain elements within main groups. In modern terms, he did not see the need to separate out the transition metals, as is now carried out in the modern medium-long form of the periodic table. (See chapter 1 for diagrams of the short and medium-long forms of the periodic table.) The law of octaves applies perfectly to the first two periods, excluding the noble gases, which had not yet been discovered. Beyond that, Newlands's periodicities were bound to run into difficulties since the inclusion of the transition metals makes the later periods much longer than 8. Only his fellow London chemist, William Odling, anticipated this problem, as described below.

Newlands first announced his law of octaves in a paper delivered to the London Chemical Society in 1866, but to his great misfortune, his insight was badly received. This event is perhaps Newlands's best-known legacy to the history of the periodic system and is repeated ad nauseam in textbooks and popular accounts. What Newlands presented to the society was an improved version of his 1865 system, in which more elements were arranged strictly according to his ordinal numbers. In his earlier published table of 1865, this had not been the case, especially for the elements with ordinal numbers beyond 50. The new table presented to the society (table 3.4) also shows some chemical improvements in that the element lead is now placed in the same group as carbon, silicon, and tin, whereas it had not appeared in the table of 1865.

As the popular story goes, Newlands included the mention of a law of octaves in his presentation and proceeded to draw an analogy with the musical scale. Whether he seriously intended to suggest a connection between chemistry and music is not clear. In any case, his fanciful analogy was probably not the reason why the chemists in attendance were quick to dismiss Newlands's scheme. Their hostility is perhaps better attributed to the British tendency, of the time, to be suspicious of theoretical ideas in general. The best-known response to Newlands is the much-quoted one of George Carey Foster, who suggested that Newlands might well have obtained a superior classification scheme if he had merely ordered the elements alphabetically according to the first letter of each of their names.

Some modern commentators have tried to exonerate Newlands by saying that he was unlucky to have been working at the time before the noble gases had been discovered. They suggest that if he had known of this additional group, he would have realized that chemical repetition follows a "nonet law," not an octet rule. In that case, he might not have been tempted to make analogies with the musical scale and thus might not have fallen prey to the assembled scientists at the London Chemical Society. These attempts to exonerate Newlands are in fact rather unnecessary, since he specifically anticipated the possibility of the repeat period being greater than 8, as discussed below.

Another aspect of the Newlands mythology concerns the fact that the chemists gathered at the London Chemical Society meeting decided not to permit publication of Newlands's article in the society's proceedings. Although this is quite true, it should not be taken to imply that Newlands was prevented from publishing his ideas on the classification of the elements. In fact, he had already published several articles in the highly respected journal *Chemical News* and would succeed in publishing the contents of his presentation to the London Chemical Society a few months later in this same journal. The reason why Newlands's ill-fated talk had been denied publication by the London Chemical Society only emerged seven years after the event, when Odling, who had chaired the meeting, wrote that the society had made it a rule not to publish papers of a purely theoretical nature, since it was likely to lead to controversy. One cannot rule out the possibility that there may have been a certain amount of rivalry between Odling and Newlands regarding the construction of periodic systems and that this may have influenced Odling's view. Nevertheless, this seems rather tenuous since Newlands was something of an outsider among academic chemists, and it is unlikely that Odling would have regarded him as a threat. Odling was a more rounded chemist whose main interests lay in the wider question of the relationship between atomic weight and equivalent weight and the related question of the difference between atoms and molecules. Unlike in the case of Newlands, the classification of the elements was only a sideline for Odling.

In an article published in 1866, Newlands tried to answer the criticisms that had been leveled at him in the course of his fateful presentation to the London Chemical Society. The accompanying table published by Newlands represents the first time that he arranged chemical groups in vertical columns, and once again, the ordering of the elements follows a numerical order with the exception of three reversals (Ce and La with Zr, U with Sn, and Te with I). Newlands responded to the criticism that he had not left any gaps and that this would be a problem when future elements were discovered:

> The fact that such a simple relation [the law of octaves] exists now, affords a strong presumptive proof that it will always continue to exist, even should hundreds of new elements be discovered. For, although the difference in the number of analogous elements might, in that case, be altered from 7, to a

TABLE 3.4

Newlands's table illustrating the law of octaves as presented to the Chemical Society in 1866.

	No.		*No.*		*No.*		*No.*		*No.*		*No.*		*No.*		*No.*
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

Note the inclusion of a number of nonconventional symbols, from the contemporary point of view. These are G for glucinium, subsequently called beryllium; Bo for boron; Di for didymium, which later turned out to be a mixture of two rare earth elements; and Ro for rhodium.

J.A.R. Newlands, as reported in Proceedings of Chemical Societies: Chemical Society, *Chemical News*, 13, 113–114, 1866, table on p. 113.

> multiple of 7, of 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the elements would be none the less evident.[28]

Newlands is, of course, correct.[29] In fact, he was vindicated by the subsequent discovery of the noble gases, which, instead of disrupting the repeating pattern, simply increased the repeat distance between successive periods to 8 rather than 7.[30] In a later system, of 1878, Newlands would carry out just such an expansion by establishing periods with 10 elements, although the net result of this change was to create far too many empty spaces that were not subsequently filled by new elements (figure 3.5).

Following the publication of Mendeleev's periodic system in 1869, Newlands began to publish a series of letters in which he attempted to establish his priority in arriving at the first successful periodic system. Meanwhile, much to his chagrin, the Davy Medal was awarded jointly to Mendeleev and Lothar Meyer in 1882 for their discovery of the periodic system. Newlands renewed his efforts, publishing a further summary of his own achievements in 1882 and again in 1884 in book form.[31] It would appear that his tenacity was at least partly rewarded when the Davy Medal was finally awarded to him in 1887. As late as 1890, Newlands published a rejoinder to a critique that Mendeleev had expressed in his Faraday lecture of two years before. It is also worth noting that, despite this critique, Mendeleev regarded the work of Newlands more highly than that of Lothar Meyer.

During the period 1863–1890, Newlands published a total of 16 articles, in which he tried many different schemes on the classification of the elements. These met with varying degrees of success both in scientific terms and in terms of recognition. There can be no doubt, however, that Newlands ranks among the true pioneers of the modern periodic system, in particular for being the first to recognize explicitly the existence of the periodic law, which in many ways is the real crux of the matter.

William Odling

Unlike many discoverers of the periodic system, who were otherwise marginal figures in the history of chemistry, William Odling was a distinguished chemist and scientist who held some very important positions in the course of his career. Most notably, he succeeded Michael Faraday as director of the Royal Institution in London. Odling also had the advantage of having attended the Karlsruhe conference, where he had given a lecture on the need to adopt a unified system of atomic weights. Unlike Newlands, whose first attempts at a periodic system were carried out in ignorance of Cannizzaro's recommended values of atomic weights, Odling was able to avail himself of these values from the beginning of his attempts at producing a table of the elements. In fact, after Karlsruhe, Odling rapidly became the leading champion of the views of Cannizzaro and Avogadro in England. Odling

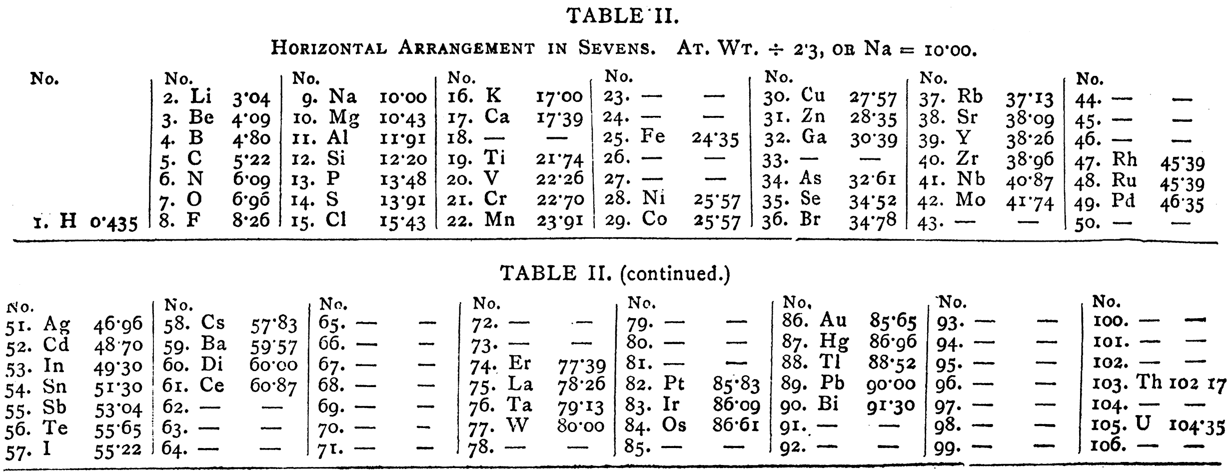


TABLE II.

HORIZONTAL ARRANGEMENT IN SEVENS. AT. WT. ÷ 2·3, OR Na = 10·00.

No.			No.			No.			No.			No.			No.			No.			No.		
			2.	Li	3·04	9.	Na	10·00	16.	K	17·00	23.	—	—	30.	Cu	27·57	37.	Rb	37·13	44.	—	—
			3.	Be	4·09	10.	Mg	10·43	17.	Ca	17·39	24.	—	—	31.	Zn	28·35	38.	Sr	38·09	45.	—	—
			4.	B	4·80	11.	Al	11·91	18.	—	—	25.	Fe	24·35	32.	Ga	30·39	39.	Y	38·26	46.	—	—
			5.	C	5·22	12.	Si	12·20	19.	Ti	21·74	26.	—	—	33.	—	—	40.	Zr	38·96	47.	Rh	45·39
			6.	N	6·09	13.	P	13·48	20.	V	22·26	27.	—	—	34.	As	32·61	41.	Nb	40·87	48.	Ru	45·39
			7.	O	6·96	14.	S	13·91	21.	Cr	22·70	28.	Ni	25·57	35.	Se	34·52	42.	Mo	41·74	49.	Pd	46·35
1.	H	0·435	8.	F	8·26	15.	Cl	15·43	22.	Mn	23·91	29.	Co	25·57	36.	Br	34·78	43.	—	—	50.	—	—

TABLE II. (continued.)

No.			No.			No.			No.			No.			No.			No.			No.		
51.	Ag	46·96	58.	Cs	57·83	65.	—	—	72.	—	—	79.	—	—	86.	Au	85·65	93.	—	—	100.	—	—
52.	Cd	48·70	59.	Ba	59·57	66.	—	—	73.	—	—	80.	—	—	87.	Hg	86·96	94.	—	—	101.	—	—
53.	In	49·30	60.	Di	60·00	67.	—	—	74.	Er	77·39	81.	—	—	88.	Tl	88·52	95.	—	—	102.	—	—
54.	Sn	51·30	61.	Ce	60·87	68.	—	—	75.	La	78·26	82.	Pt	85·83	89.	Pb	90·00	96.	—	—	103.	Th	102 17
55.	Sb	53·04	62.	—	—	69.	—	—	76.	Ta	79·13	83.	Ir	86·09	90.	Bi	91·30	97.	—	—	104.	—	—
56.	Te	55·65	63.	—	—	70.	—	—	77.	W	80·00	84.	Os	86·61	91.	—	—	98.	—	—	105.	U	104·35
57.	I	55·22	64.	—	—	71.	—	—	78.	—	—	85.	—	—	92.	—	—	99.	—	—	106.	—	—

FIGURE 3.5 Table of 1878. J.A.R. Newlands, On Relations Among the Atomic Weights of the Elements, *Chemical News*, 37, 255–258, 1878, pp. 256–257.

above all others would therefore have recognized the significance of the new atomic weight values.

Odling's main article on the periodic system appeared in 1864, while he was a reader in chemistry at St. Bartholomew's Hospital in London. Whereas Newlands's system of the same year had only included 24 of the 60 known elements, Odling succeeded in including 57 of them (figure 3.6). Furthermore, Odling's paper preceded Newlands's announcement of periodicity to the London Chemical Society, which was made shortly afterward in 1865. Nevertheless, it appears that the two chemists worked quite independently of each other.

Odling begins his article by stating, "Upon arranging the atomic weights or proportional numbers of the sixty or so recognized elements in order of their several magnitudes, we observe a marked continuity in the resulting arithmetical series,"[32] and he goes on to point out a few exceptions to this regularity. Then he makes an observation that amounts to an independent discovery of the periodic system:

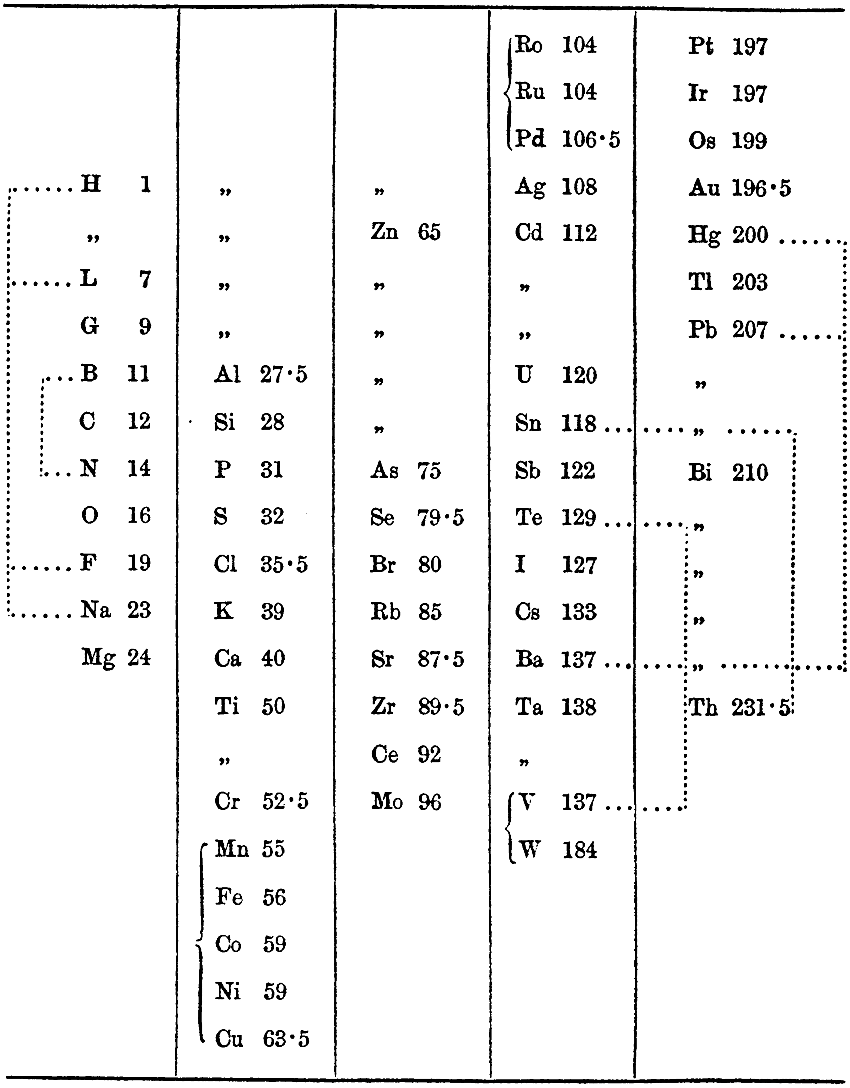
> With what ease this purely arithmetical seriation may be made to accord with a horizontal arrangement of the elements according to their usually received groupings, is shown in the following table, in the first three columns of which the numerical sequence is perfect, while in the other two the irregularities are but few and trivial.[33]

That Odling had recognized the periodicity in chemical properties is clearly seen in the horizontal groupings that he organizes in this table.

Odling notes that there are a considerable number of pairs of chemically analogous elements, indeed, half of all the known elements, whose difference in atomic weights lies between the values of 84.5 and 97. Some of these pairs are shown in table 3.5. He then notices that about half of these cases include the first and third members of previously known triads. He suggests that a middle member might be found for the other half, stating that "the discovery of intermediate elements in the case of some or all of the other pairs is not altogether improbable."[34] This is clearly an example of a prediction made on the basis of a periodic system, although admittedly a rather tentative one that was not further developed with specific examples.

A table is then given of as many as 17 pairs of elements whose members differ by atomic weights of 40–48 (table 3.6). This is followed by yet a third set of pairs of elements, 10 instances in all, of "more or less analogous elements" that differ in atomic weight by 16 units, or something close to this amount. It is worth noting perhaps, that in 7 out of these 10 instances, the element with the lower atomic weight of the pair is the first member of the group of similar chemical elements to which they both belong.

It would appear that, in identifying these gaps, Odling was making a rather remarkable observation that seemed to go beyond the earlier triadic relationships, since the 16-unit gap appears with approximate consistency in so many of Odling's



			Ro 104	Pt 197
			Ru 104	Ir 197
			Pd 106·5	Os 199
H 1	”	”	Ag 108	Au 196·5
”	”	Zn 65	Cd 112	Hg 200
L 7	”	”	”	Tl 203
G 9	”	”	”	Pb 207
B 11	Al 27·5	”	U 120	”
C 12	Si 28	”	Sn 118	”
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79·5	Te 129	”
F 19	Cl 35·5	Br 80	I 127	”
Na 23	K 39	Rb 85	Cs 133	”
Mg 24	Ca 40	Sr 87·5	Ba 137	”
	Ti 50	Zr 89·5	Ta 138	Th 231·5
	”	Ce 92	”	
	Cr 52·5	Mo 96	V 137	
	Mn 55		W 184	
	Fe 56			
	Co 59			
	Ni 59			
	Cu 63·5			

FIGURE 3.6 Table of 1864. W. Odling, On the Proportional Numbers of the Elements, *Quarterly Journal of Science*, 1, 642–648, 1864, p. 643.

three sets of element pairs. One might claim that just this observation constitutes the recognition of periodicity. What Odling appears to have realized, particularly in the case of the last set of elements, is that, in as many as 10 important cases, there is an approximate repetition in the properties of any of these elements following a difference in atomic weight of 16, or very close to this value. Bearing in mind that he used atomic weights, which are approximately double the values of atomic

TABLE 3.5
Odling's first table of differences.

I	–	Cl	or	127	–	35.5	=	91.5
Au	–	Ag		296.5	–	108	=	88.5
Ag	–	Na		108	–	23	=	85
Cs	–	K		133	–	39	=	97

Based on W. Odling, On the Proportional Numbers of the Elements *Quarterly Journal of Science*, 1, 642–648, 1864, table on p. 644.

number, we see that this is also very close to being the recognition of the law of octaves. In other words, Odling appears to have realized that the repetition occurs after a difference in atomic number of eight units, which corresponds to an atomic weight difference of 16.

Odling makes the further claim that the chemical similarities between elements separated by differences of about 48 in atomic weight, such as cadmium and zinc, are greater than those between pairs of elements, such as zinc and magnesium, that are separated by other intervals, such as 41 in this case. Thus, it would appear that he recognized the need to separate certain elements (those that would eventually become known as the transition metals) from the main body of the table. In this way, periodicity could be retained in the properties of the majority of the elements, as is done in the modern medium-long form of the table.[35] If the transition metals are separated out of the short-form table, the primary periodic relationship between main-group elements is emphasized and the fact that period lengths vary is accommodated in a natural manner.

TABLE 3.6
Odling's third table of differences.

Cl	–	F	or	35.5	–	19	=	16.5
K	–	Na		39	–	23	=	16
Na	–	Li		23	–	7	=	16
Mo	–	Se		96	–	80	=	16
S	–	O		32	–	16	=	16
Ca	–	Mg		40	–	24	=	16
Mg	–	G		24	–	9	=	15
P	–	N		31	–	14	=	17
Al	–	B		27.5	–	11	=	16.5
Si	–	C		28	–	12	=	16

W. Odling, On the Proportional Numbers of the Elements, *Quarterly Journal of Science*, 1, 642–648, 1864, table on p. 645.

It so happens that Odling was correct in this case. From the perspective of the modern periodic table, cadmium and zinc are both transition metals that show a primary kinship, whereas zinc and magnesium belong to the transition metals and main-group elements, respectively, and show only secondary kinships. Odling may have anticipated the modern trend to separate zinc and magnesium into different groups and, indeed, different blocks of the periodic table.

Any claim that Odling is making a significant anticipation here is vitiated, however, by the fact that in the same paragraph he goes on to give what he considers to be other examples of this behavior, all of which are incorrect. He claims that there is a greater chemical similarity among cesium, rubidium, and potassium, as well as among barium, strontium, and calcium, both of which sets show common differences of about 48 between closest members, than between potassium and sodium, where the difference is only 18. This is simply not the case.

If we are to judge these suggestions from the perspective of the modern table, we see that Odling is correct in drawing the first distinction, given that magnesium does not belong with the transition elements zinc and cadmium. However, in the second example, it has turned out that no comparable difference exists between potassium and sodium, both of which are now classified as main-group elements of group I. In any case, separating the transition metals from the main body of the table would not affect any of these groupings, as they are all composed of main-group elements.

What is confusing the issue, as far as the numerical relationships are concerned, is precisely the fact that successive periods in the mature periodic table do not all have the same length. Odling does not appear to have realized that different periods have different lengths, even though he has deliberately separated some elements out from the main body of the table. The suggestion that Odling anticipated the existence of transition metal groups in the periodic table to preserve periodicity is thus somewhat debatable.[36]

Gustavus Hinrichs

The case of Gustavus Hinrichs is rather unusual among the discoverers of the periodic system. This is because his scientific interests were so far ranging, and the evidence he brought to bear on producing a classification of the elements was so diverse, as to lead some commentators to regard him as a mere crank. Although he held a number of academic appointments, first at the University of Iowa and later at the University of Missouri–St. Louis, Hinrichs seemed to go out of his way to cultivate eccentricity. In addition, he seldom gave references to other authors in his numerous publications, thus making a balanced assessment of his contributions rather more difficult.

Hinrichs was born in 1836 in Holstein, which was then a part of Denmark but later became a German province. Hinrichs published his first book at the age of 20, while attending the University of Copenhagen. He immigrated to the United States in 1861 to escape political persecution and, after a year of teaching high school, was appointed head of Modern Languages at the University of Iowa. A mere one year later, he became Professor of Natural Philosophy, Chemistry, and Modern Languages. He is also credited with founding the first meteorological station in the United States in 1875, acting as its director for 14 years.

Hinrichs was a prolific author who published some 3000 articles in Danish, French, and German, as well as in English, in addition to about 25 books of varying lengths in English and German. These books include the highly eccentric *Atomechanik* of 1867, in German, in which Hinrichs gives his definitive views on the classification of the elements. It is interesting to note that the majority of Hinrichs's articles were published in languages other than English. He seems to have disliked American journals, complaining that their insistence on correcting his work caused unacceptable delays in publication. Karl Zapffe, the author of a detailed analysis of Hinrichs's work, has suggested that Hinrichs's disaffection with American journals may have been part of his distaste for all things American. This may have included his American colleagues and may have led to his eventual dismissal from the University of Iowa in 1885.[37]

As Zapffe writes:

> It is not necessary to read far into Hinrichs' numerous publications to recognize the marks of an egocentric zeal which defaced many of his contributions with an untrustworthy eccentricity. Only at this late date does it become possible to separate those inspirations which were real—and which swept him off his feet—from background material which was captured in the course of his own learning. Whatever the source, Hinrichs usually dressed it with multilingual ostentation, and to such a point of disguise that he even came to regard Greek philosophy as his own.[38]

The jury is still out on Hinrichs. While Jan van Spronsen includes him in his list of six genuine discoverers of the periodic system, William Jensen, a chemist and chemical educator at the University of Cincinnati, is among those who regard Hinrichs as a scientific maverick and a crank.[39] This also seems to be the conclusion of Heinz Cassebaum and George Kauffman, who include just six lines on Hinrichs in an article on the codiscoverers of the periodic system and who devote considerable space to a footnote pointing out his unconventional scientific attitudes.[40] But careful consideration of Hinrichs's work shows that it embodied much useful science, if one is prepared to take time to examine the various strands of his research.

Hinrichs took a rather Pythagorean approach to science in that he was captivated by numerical relationships, even those involving very diverse phenomena. Whereas Pythagoreanism had already figured in the early research on triads and

Prout's hypothesis, Hinrichs's own brand of Pythagoreanism was far more extreme. By an ingenious argument (examined shortly below), he was led to postulate the notion that atomic spectra can provide information on the dimensions of atoms, an idea that is essentially correct from the modern perspective.[41] Since Hinrichs's idea has not been clearly described in previous accounts of the evolution of the periodic system, or at least the few accounts that even mention his work, I attempt to describe it here.

Hinrichs's wide range of interests extended to astronomy. Like many authors before him, as far back as Plato, Hinrichs noticed some numerical regularities regarding the sizes of the planetary orbits. In an article published in 1864, Hinrichs showed a table (table 3.7) that he proceeded to interpret. He expressed the differences in these distances by the formula $2^x \times n$, in which n is the difference in the distances of Venus and Mercury from the sun, or 20 units. Depending on the value of x, the formula therefore gives the following distances:[42]

$$\begin{gathered}2^0 \times 20 = 20\\ 2^1 \times 20 = 40\\ 2^2 \times 20 = 80\\ 2^3 \times 20 = 160\\ 2^4 \times 20 = 320\\ \text{etc.}\end{gathered}$$

A few years previously, in 1859, the Germans Gustav Robert Kirchhoff and Robert Bunsen had discovered that each element could be made to emit light, which

Table 3.7
Hinrichs's 1864 table of planetary distances.

	Distance to the Sun
Mercury	60
Venus	80
Earth	120
Mars	200
Asteroid	360
Jupiter	680
Saturn	1,320
Uranus	2,600
Neptune	5,160

G.D. Hinrichs, The Density, Rotation and Relative Age of the Planets, *American Journal of Science and Arts*, 2(37), 36–56, 1864, table on p. 43.

could then be dispersed with a glass prism and analyzed quantitatively.[43] They also discovered that every single element gave a unique spectrum consisting of a set of specific spectral lines, which they set about measuring and publishing in elaborate tables. Some authors suggested that these spectral lines might provide information about the various elements that had produced them, but these suggestions met with strenuous criticism from one of their discoverers, Bunsen. Indeed, Bunsen remained quite opposed to the idea of studying spectra in order to study atoms or to classify them in some way.[44]

Hinrichs, however, had no hesitation in connecting spectra with the atoms of the elements. In particular, he became interested in the fact that, with any particular element, the frequencies of its spectral lines always seemed to be whole number multiples of the smallest difference. For example, in the case of calcium, a ratio of 1:2:4 had been observed among its spectral frequencies. Hinrichs's interpretation of this fact was bold and elegant: If the sizes of planetary orbits produce a regular series of whole numbers, and if the ratios among spectral line differences also produce whole number ratios, the cause of the latter might lie in the size ratios among the atomic dimensions of the various elements (table 3.8). This is Pythagoreanism with a vengeance, but it proved to be fruitful in that it led Hinrichs to a successful, and highly novel, means of classifying the elements into a periodic system.

By closely studying the work of Kirchhoff and Bunsen, Hinrichs found that some of the spectral line frequencies, those referred to as "dark lines," could be related to the chemistry of the elements through their atomic weights, as well as to their postulated atomic dimensions. The difference between the spectral line frequencies seemed to be inversely proportional to the atomic weights of the elements in question. Hinrichs quoted the values of calcium, where the frequency difference is 4.8 units, and barium, which is chemically similar but has a higher atomic weight and shows a frequency difference of 4.4 units.[45]

Hinrichs then proposed the following formula to connect the atomic weight of any element with its atomic dimensions:

$$A = a \times b \times c$$

A is the atomic weight and *a*, *b*, and *c* are the respective lengths of the sides of a prism denoting the shape of the atom. The base of the prism, which is taken as the dimension *a*, would be of the same size for all the elements belonging to a particular

TABLE 3.8
Schematic form of Hinrichs's argument.

From astronomy	Size ratios among orbits	→	Whole number ratios
From spectra	Observation of whole number ratios	→	Size ratios among atomic dimensions

chemical group. If a particular group contained square prisms, their formula would reduce to

$$A = a^2 \times b$$

In other cases, where the base of the prism took on a triangular shape, the formula would be expressed as

$$A = \left(a \times b \times c\right) + k,$$

where *k* is a constant. Given how improbable this whole approach might seem, it is quite remarkable how useful it turned out to be when Hinrichs applied it to rationalizing the atomic weights of the elements.[46] For example, it served quite successfully as a basis for deciding which elements should be grouped together in his

TABLE 3.9
Hinrichs's table of atomic weights and atomic dimensions for several groups of elements.

	n	*A*	*Calculated*	*Determined*	*Difference*
Oxygen group: quadratic formula			$A = n \times 4^2$		
Oxygen	1	1×4^2	= 16	16	0.0
Sulfur	2	2×4^2	= 32	32	0.0
Selenium	5	5×4^2	= 80	80	0.0
Tellurium	8	8×4^2	= 128	128	0.0
Alkali metal group: quadratic with pyramid			$A = 7 + (n \times 4^2)$		
Lithium	0	7	7	0.0	
Sodium	1	$7 + (1 \times 4^2)$	= 23	23	0.0
Potassium	2	$7 + (2 \times 4^2)$	= 39	39	0.0
Rubidium	5	$7 + (5 \times 4^2)$	= 87	85.4	− 1.6
Cesium	8	$7 + (8 \times 4^2)$	= 135	133	− 2.0
Chlorine group: quadratic formula			$A = (n \times 3^2) \pm 1$		
Fluorine	2	$(2 \times 3^2) + 1$	= 19	19	0.0
Chlorine	4	$(4 \times 3^2) - 1$	= 35	35.5	+ 0.5
Bromine	9	$(9 \times 3^2) - 1$	= 80	80	0.0
Iodine	14	$(14 \times 3^2) + 1$	= 127	127	0.0
Alkaline earth group: quadratic formula			$A = n \times 2^2$		
Magnesium	3	3×2^2	= 12	12	0.0
Calcium	5	5×2^2	= 20	20	0.0
Strontium	11	11×2^2	= 44	43.8	− 0.2
Barium	17	17×2^2	= 68	68.5	+ 0.5

Remade from G.D. Hinrichs, On the Spectra and Composition of the Elements, *American Journal of Science and Arts*, 92, 350–368, 1866, table on p. 365.

periodic system. Table 3.9 shows some of his groups and demonstrates how in each case one of the formulas given above is able to accommodate, rather accurately, the atomic weight of each element in the proposed groups. Of course, this was not the only reason Hinrichs grouped elements together. Many of the groupings suggested themselves primarily on the basis of chemical similarities, with which Hinrichs would have been well acquainted through his knowledge of chemistry.

In the course of this work, Hinrichs expressed his support for the notion of primary matter, which had been the basis of Prout's hypothesis of half a century earlier. Hinrichs was convinced that the atomic weights of the elements were whole numbers. Because the value of chlorine was 35.5 according to Cannizzaro's atomic weights, Hinrichs concluded that the primary atom had a weight of half the value of hydrogen, and so he took H/2 to be the basic unit for expressing all the other weights. The weight of chlorine therefore assumed a value of 71, and the Cannizzaro atomic weights of all the other elements were similarly doubled. These are the values that are seen in the culmination of Hinrichs's work on the classification of the elements, his spiral periodic system, as shown in figure 3.7.

The 11 "spokes" radiating from the center of this wheel-like system consist of three predominantly nonmetal groups and eight groups containing metals. From a modern perspective, the nonmetal groups appear to be incorrectly ordered, in that the sequence is groups VI, V, and then VII when proceeding from left to right at the top of the spiral. Hinrichs classes the group containing carbon and silicon with the metallic groups, presumably because it also includes the metals nickel, palladium, and platinum. In the modern table, these three metals are indeed grouped together, but not in the same group as carbon and silicon, which belong with germanium, tin, and lead in group IV.

Overall, however, Hinrichs's periodic system is rather successful in grouping together many important elements. One of its main advantages is the clarity of its groupings, compared, say, with Newlands's more elaborate but less successful periodic systems in 1864 and 1865. For example, Hinrichs groups together oxygen, sulfur, selenium, and tellurium. Newlands also groups these elements together but includes osmium (Os) with them. Hinrichs groups together nitrogen, phosphorus, arsenic, antimony, and bismuth. So does Newlands, but he incorrectly includes manganese, as well as didymium[47] and molybdenum, in one space. Hinrichs groups together lithium, sodium, potassium, and rubidium. Newlands also groups these elements together but also incorrectly includes copper, silver, gold, and tellurium.[48]

Although it is not arranged as a long-form table, Hinrichs's classification seems to capture many of the primary periodicity relationships seen in the modern periodic table, and unlike many of Newlands's tables, it is not cluttered by attempts to show secondary kinship relationships. Hinrichs, for example, groups together copper, silver, and gold. In the case of Newlands, these elements are grouped separately, with the exception of one table in 1865, which classifies the three elements together and also intersperses them with such other elements as potassium, rubidium, and cesium.[49]

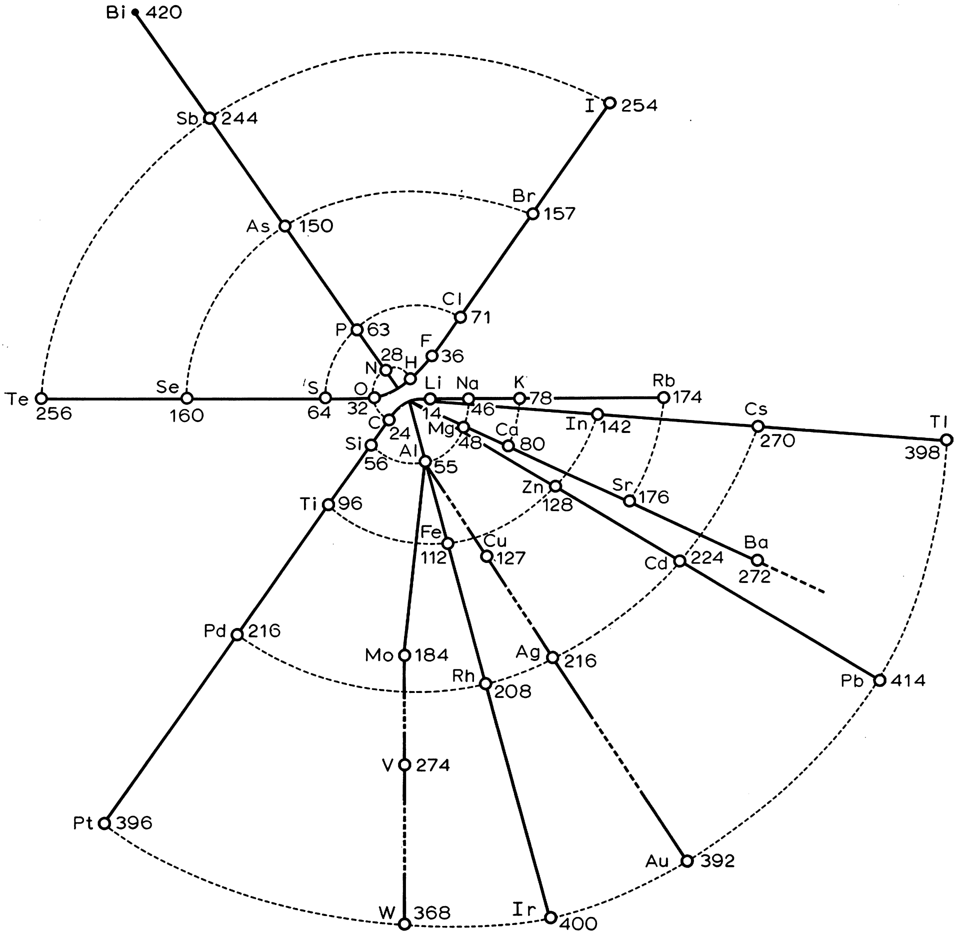


FIGURE 3.7 Hinrichs's spiral periodic system of 1867. G.D. Hinrichs, *Programm der Atomechanik oder die Chemie eine Mechanik de Pantome*, Augustus Hageboek, Iowa City, IA, 1867. As simplified by J. van Spronsen, *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969 (by permission from Elsevier).

It is clear from his books that Hinrichs possessed a deep knowledge of chemistry, as well as a proficiency in mineralogy.[50] Yet his approach to the classification of the elements was only partly chemical. He was perhaps the most interdisciplinary of all the discoverers of the periodic system. Indeed, the fact that Hinrichs arrived at his system from such a different direction as the others might be taken to lend the periodic system itself independent support, just as Lothar Meyer's studies of physical periodicity (described below) also do.

In an article published in *The Pharmacists* in 1869,[51] Hinrichs discusses previous unsuccessful attempts to classify the elements, but in doing so fails to mention any of his codiscoverers, such as De Chancourtois, Newlands, Odling, Lothar Meyer, and Mendeleev. Indeed, Hinrichs characteristically appears to have completely ignored all other attempts to base the classification of the elements directly on atomic weights, though one can assume that he was aware of them given his knowledge of foreign languages. This is not to say that his classification is unconnected with atomic weights, only that the connection is rather indirect in view of the astronomical argument that seems to be the basis of the approach.

Finally, it should be stressed that Hinrichs appeared to be ahead of his time in assigning great importance to analysis of the spectra of the elements and in trying to relate these facts to the periodic classification. However, his spectral studies are by no means universally accepted. Some contemporary historians, including Klaus Hentschel, have criticized Hinrichs's work, claiming that he was somewhat selective in what data he admitted into his calculations.[52]

More than that of any other scientist discussed in this book, the work of Hinrichs is so idiosyncratic and labyrinthine that a more complete study of all his work will be required before anyone can venture to pronounce on its real value.

Julius Lothar Meyer

Julius Lothar Meyer (figure 3.8) was born in 1830 in Heilbronn, Germany. He was the fourth of seven children of a physician father and a mother whose own father was also a local physician. Julius and one of his brothers, Oskar, began their studies with the intention of continuing this family medical tradition, but it was not long before both of them had turned to other fields. Oskar became a physicist, while Julius became one of the most influential chemists of his time.

FIGURE 3.8
Julius Lothar Meyer. Photo from author's collection, permission from Edgar Fahs Smith Collection.

Lothar Meyer is best remembered for his independent discovery of the periodic system, although more credit is invariably accorded to Mendeleev. The two chemists eventually became engaged in a rather bitter priority dispute, which Mendeleev apparently won, although how much of that was due to Mendeleev's more forceful personality is difficult to ascertain fully. Certainly, Mendeleev had a more complete system and went on to make predictions on the basis of his system. He was also to champion the cause of the periodic law to a far greater extent than was Lothar Meyer. But if one asks the question of who arrived at the mature periodic system first, a strong case can be made for saying that in many crucial details the system of Lothar Meyer was not only first but also more correct.

Lothar Meyer attended the Karlsruhe conference in 1860 and learned firsthand of Cannizzaro's groundbreaking work on the atomic weights of the elements.[53] He then edited a version of Cannizzaro's article that appeared in Germany in Wilhelm Ostwald's series under the title *Klassiker der Wissenschaften*. Lothar Meyer later described the effect that Cannizzaro's article had on him by saying, "[T]he scales fell from my eyes and my doubts disappeared and were replaced by a feeling of quiet certainty."[54] In 1864, Lothar Meyer published the first edition of a chemistry textbook, *Die Modernen Theorien der Chemie*, which was deeply influenced by the work of Cannizzaro. The book appeared in five editions and was translated into English, French, and Russian, eventually becoming one of the most authoritative treatments on the theoretical principles of chemistry before the advent of physical chemistry in the late 1800s.

By the time Lothar Meyer had written the manuscript for his book in 1862, he had produced a table of 28 elements arranged in order of increasing atomic weight. An adjacent table containing a further 22 elements also appeared in the book, although these were not arranged according to atomic weight order. All this took place only two years after the Karlsruhe conference. It should perhaps be noted in passing that it took Mendeleev something like nine years from the time of his attending the same conference before he, too, produced a table of elements arranged in order of increasing atomic weights.

Lothar Meyer was also deeply influenced by the work of Johann Döbereiner and Max Pettenkofer, both of whom, as described in chapter 2, had published articles on the existence of triads of elements, where the weight of the middle member was the approximate mean of that of the flanking elements. Going further, Pettenkofer had pointed to an analogy between the regular increase in the weights of successive members of any homologous series in organic chemistry and the almost regular increase in the atomic weights of similar elements within any triad, something that had also been noticed by Dumas.

Most organic compounds can be classified according to the homologous series to which they belong. Such series are created in an iterative fashion with the repeated addition of a chemical unit, such as CH_2 in the case of the alkanes.[55] This regularity suggested to Pettenkofer and Dumas that the molecules of such series must be composed of regular units.

If the analogy between these organic compounds were also applied to inorganic atoms, it would suggest that atoms are likewise composed of parts. In other words, just as the regularity in the increasing molecular weights in a homologous series suggests that its members contain some sort of building block universal to that series, so the regularity seen in the intervals between atomic weights of members of a triad would suggest that the atoms of those members are somehow modular. Lothar Meyer did indeed regard such evidence as pointing to the composite nature of inorganic atoms,[56] something that Mendeleev never accepted throughout his life.[57]

Lothar Meyer published his table of 28 elements for the first time in 1864 (figure 3.9). His arrangement of elements in order of increasing atomic weights and the clear establishment of horizontal relationships among these elements are other instances in which Lothar Meyer anticipated Mendeleev by several years.[58] As described in chapter 4, where we encounter the details of Mendeleev's work, this recognition of the need to order the elements in terms of increasing atomic weight, and especially the recognition of horizontal relationships, has wrongly been regarded as a first by Mendeleev. Yet here in 1864, Lothar Meyer is publishing both ideas simultaneously, without, in most cases, receiving due recognition for these advances from contemporary, or later, commentators.

Lothar Meyer's 1864 table also showed clearly for the first time a regular variation in valency of the elements, from 4 to 1 on moving from left to right across the table, followed by a repetition of valence 1 and a further increase to elements with valence 2.[59] This table suggests that Lothar Meyer struggled to arrange elements in terms of atomic weight as well as chemical properties. He seems to have decided to let chemical properties outweigh strict atomic weight ordering in some cases. An example of this is in his grouping of tellurium with elements such as oxygen and sulfur, while iodine is grouped with the halogens, in spite of their ordering according to atomic weight. Lothar Meyer also separated the elements into two tables in a manner corresponding to the separation of our modern main-group elements from the modern transition elements. As mentioned above in the case of Odling, such a separation has become a feature of the modern medium-long-form and long-form tables.

Another noteworthy feature of Lothar Meyer's table of 1862 (published in 1864) is the presence of many gaps to denote unknown elements. Once again, it appears that the leaving of gaps did not originate with Mendeleev, who was to wait a further five years before even venturing to publish a periodic system and eventually making the detailed predictions for which he subsequently became so well known. Lothar Meyer's table contains interpolations between neighboring elements. In the space below the element silicon, for example, he indicates that there should be an element whose atomic weight would be greater than silicon's by a difference of 44.55. This implies an atomic weight of 73.1 for this unknown element, which when discovered was found to have an atomic weight of 72.3. This

	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
	——	——	——	——	Li = 7.03	(Be = 9.3?)
Differenz =	——	——	——	——	16.02	(14.7)
	C = 12.0	N = 14.04	O = 16.00	Fl = 19.0	Na = 23.05	Mg = 24.0
Differenz =	16.5	16.96	16.07	16.46	16.08	16.0
	Si = 28.5	P = 31.0	S = 32.07	Cl = 35.46	K = 39.13	Ca = 40.0
Differenz =	$\frac{89.1}{2}$ = 44.55	44.0	46.7	44.51	46.3	47.6
	——	As = 75.0	Se = 78.8	Br = 79.97	Rb = 85.4	Sr = 87.6
Differenz =	$\frac{89.1}{2}$ = 44.55	45.6	49.5	46.8	47.6	49.5
	Sn = 117.6	Sb = 120.6	Te = 128.3	I = 126.8	Cs = 133.0	Ba = 137.1
Differenz =	89.4 = 2 x 44.7	87.4 = 2 x 43.7	——	——	(71 = 2 x 35.5)	——
	Pb = 207.0	Bi = 208.0	——	——	(Tl = 204?)	——

FIGURE 3.9 Table of 1864. J. Lothar Meyer, *Die modern thoerien und ihre Bedeutung fur die chemische Statisik*, Breslau (Wroclaw), 1864, p. 135.

prediction of the element germanium, which was first isolated in 1886, is usually attributed to Mendeleev, even though it was clearly anticipated by Lothar Meyer in this early table of 1864.

The criticism has been made that Lothar Meyer did not explicitly refer to atomic weight in his 1864 table.[60] This objection seems a little excessive, however, since with regard to the 28-element table, the arrangement is clearly based on increasing atomic weight, such that Lothar Meyer may not have felt the need to comment on this rather obvious feature. Of course, the same cannot be said for the smaller table consisting of 22 elements. But the fact that these elements have been separated from the other 28 may indicate that Lothar Meyer realized that in these cases the concept of increasing atomic weight did not apply strictly to the classification he chose to adopt.[61] Nevertheless, atomic weight increases vertically down each column, and there are only six inconsistencies in the increase in atomic weight going across the table. Given that Lothar Meyer had classified a total of 50 elements while showing only six mistaken reversals in atomic weights, all of which occur among the problematic transition metals (in the modern usage of the term),[62] this cannot be considered a significant failing on his part. Indeed, the only serious misplacements he made in terms of atomic weight increase concern just two elements, molybdenum and vanadium. All of his other reversals are quite within the possible bounds of error in measured atomic weights.

But perhaps Lothar Meyer's greatest strength lay in his additional knowledge of physical properties and his use of them in constructing representations of the periodic system. He paid close attention to atomic volumes, densities, and fusibilities of the elements, for example. His published diagram showing the periodicity among atomic volumes of the elements (i.e., atomic weight divided by specific gravity), in particular, is generally considered to have contributed favorably to the general acceptance of the periodic system (figure 3.10). Indeed, one can see the periodicity among the elements almost at a glance from this diagram. Mendeleev, too, was aware of the importance of atomic volume. In fact, he made predictions on atomic volumes beginning in his first article of 1869. But he did not emphasize the periodicity in this physical property of atoms, nor did he display such suggestive diagrams of its trend.

The Remelé-Seubert Episode: The Unpublished Table of 1868

In the course of the controversy between Mendeleev and Lothar Meyer, which followed the publication of their respective periodic systems, it seems fair to say that Mendeleev was the victor at least as far as the scientific public was concerned. However, there is a rather intriguing episode that did not come to light until much later and that might have made a significant difference in this controversy had it

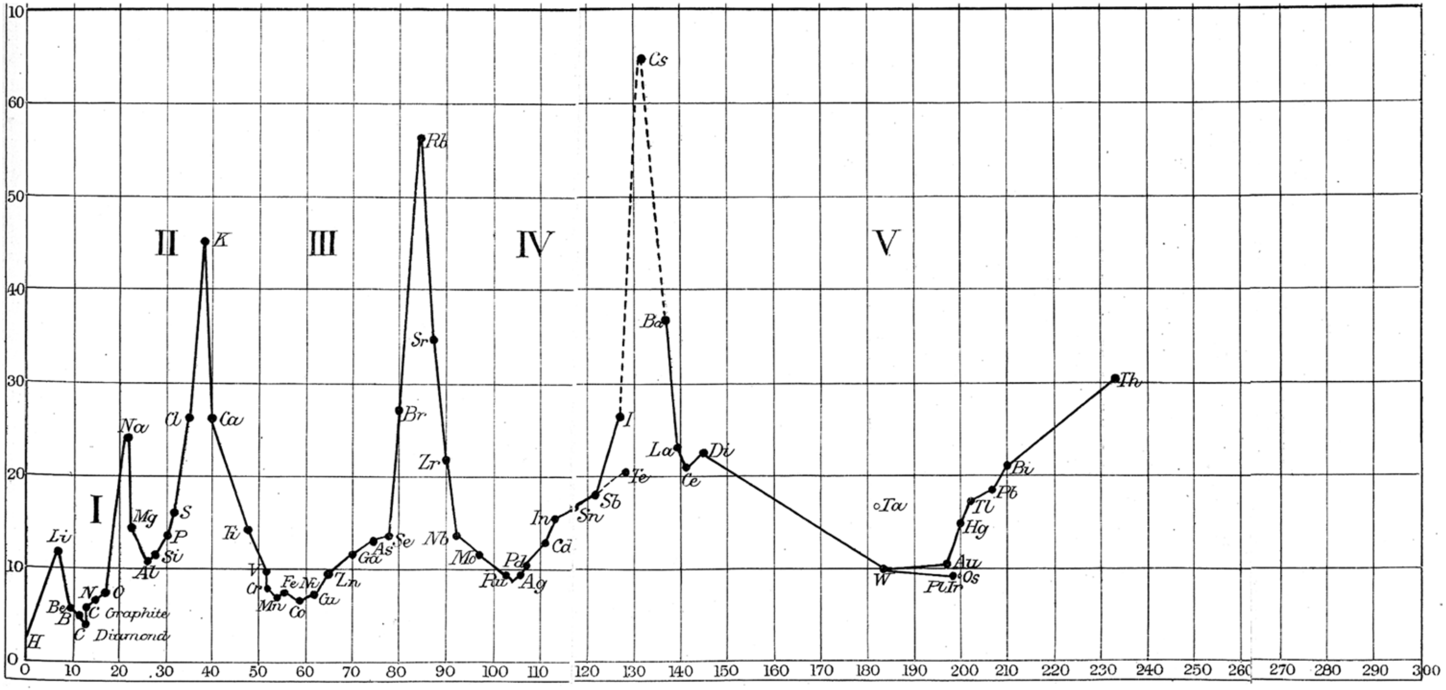
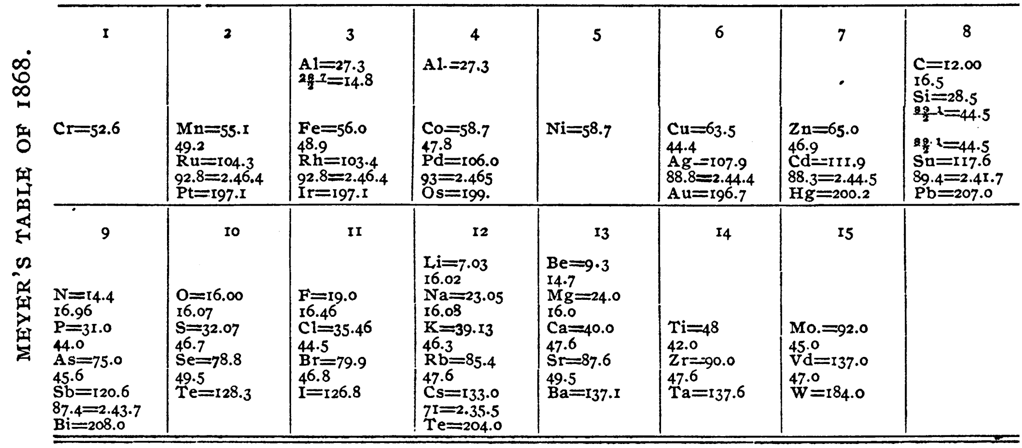


FIGURE 3.10 Plot of atomic volume versus atomic weight. J. Lothar Meyer, Die Natur der Chemischen Elemente als Function ihrer Atomgewichte, *Annalen der Chemie, Supplementband*, 7, 354–364, 1870. Redrawn by T. Bayley, Philosophical Magazine, 13, 26-37- 1882. Figure from p. 26.



MEYER'S TABLE OF 1868.

1	2	3	4	5	6	7	8
		Al=27.3 $\frac{28.7}{2}$=14.8	Al.=27.3				C=12.00 16.5 Si=28.5 $\frac{89.1}{2}$=44.5
Cr=52.6	Mn=55.1 49.2 Ru=104.3 92.8=2.46.4 Pt=197.1	Fe=56.0 48.9 Rh=103.4 92.8=2.46.4 Ir=197.1	Co=58.7 47.8 Pd=106.0 93=2.465 Os=199.	Ni=58.7	Cu=63.5 44.4 Ag=107.9 88.8=2.44.4 Au=196.7	Zn=65.0 46.9 Cd=111.9 88.3=2.44.5 Hg=200.2	$\frac{89.1}{2}$=44.5 Sn=117.6 89.4=2.41.7 Pb=207.0
9	10	11	12	13	14	15	
N=14.4 16.96 P=31.0 44.0 As=75.0 45.6 Sb=120.6 87.4=2.43.7 Bi=208.0	O=16.00 16.07 S=32.07 46.7 Se=78.8 49.5 Te=128.3	F=19.0 16.46 Cl=35.46 44.5 Br=79.9 46.8 I=126.8	Li=7.03 16.02 Na=23.05 16.08 K=39.13 46.3 Rb=85.4 47.6 Cs=133.0 71=2.35.5 Te=204.0	Be=9.3 14.7 Mg=24.0 16.0 Ca=40.0 47.6 Sr=87.6 49.5 Ba=137.1	Ti=48 42.0 Zr=90.0 47.6 Ta=137.6	Mo.=92.0 45.0 Vd=137.0 47.0 W=184.0	

FIGURE 3.11 Unpublished system of 1868. J. Lothar Meyer, 2nd ed., Breslau (Wroclaw), 1872, p. 294 (publication delayed for 4 years).

become known earlier. In 1868, when Lothar Meyer was preparing the second edition of his book, he produced a vastly expanded periodic system that included a further 24 elements and nine new vertical families of elements (figure 3.11). This system preceded Mendeleev's famous table of 1869 that subsequently claimed all the glory. Moreover, Lothar Meyer's system was more accurate than Mendeleev's. For example, Lothar Meyer correctly placed mercury with cadmium and lead with tin. In both of these cases, Mendeleev's table failed to make this connection.[63]

It appears that for some reason Lothar Meyer's 1868 table was not published. A full 25 years later, Adolf Remelé, a German chemist who succeeded Lothar Meyer as professor of chemistry in Eberswalde, showed the table to Lothar Meyer, who in the meantime seemed to have forgotten all about its existence. In 1895, after Lothar Meyer's death, Carl Seubert, one of his colleagues, finally published the forgotten table. Unfortunately, this attempt to restore some semblance of priority to Lothar Meyer, after this almost comical time delay, fell largely on deaf ears.

Conclusion

As I hope to have shown in this chapter, the periodic system developed through a process of gradual evolution rather than revolution, especially after Cannizzaro had published an accurate set of atomic weights. The discovery was made, essentially independently, by six diverse scientists who differed greatly in their fields of expertise and in their approaches. De Chancourtois, a French geologist, was unlucky to produce a rather complicated three-dimensional representation that suffered further at the hands of his publisher. But the fact remains that he made the first discovery of periodicity. In addition, many chemical mistakes led to the almost complete oblivion of his system. An English sugar chemist, Newlands, was the first to recognize the lawlike status of chemical periodicity but was somewhat ignored because, among other things, he compared periodicity to musical octaves. A more established English chemist, Odling, also designed successful periodic systems, but somewhat surprisingly denied the lawfulness of chemical periodicity. Hinrichs, a polymath working in the United States, developed a spiral periodic system using an extravagant form of Pythagoreanism in which he compared the dimensions of the solar system to the dimensions within the atom. Then came the fully mature periodic systems of Lothar Meyer and Mendeleev, two established chemistry professors in Germany and Russia, respectively, both of whom were engaged in writing chemistry textbooks. Lothar Meyer appears to have placed greater emphasis on physical properties of the atoms but hesitated to make predictions. Mendeleev, meanwhile, was the consummate chemist, familiar with the detailed chemical behavior of all the known elements and, as described in chapter 4, also ventured to make bold predictions concerning yet undiscovered elements.

Notes

1. In saying this, I am essentially agreeing with Jan van Spronsen's analysis of the developments (chapter 5). I am also following van Spronsen rather faithfully in saying that there were six discoverers. However, I would *not* want to emphasize the occurrence of definite periods in the history of the discovery of the periodic system, as van Spronsen seems to favor. I have accepted his terms "precursors" and "discoverers" partly as a means of presenting the material in a more coherent fashion. It must be realized that this is something of a conventionalist strategy and not meant to be taken too literally. The development of the periodic table, as in so many other scientific developments, took place in an evolutionary rather than a revolutionary fashion, although there may have been occasional spurts within the unfolding story.

2. L.M. Ampère, Lettre de M. Ampère à M. le comte Berthollet, sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre et la disposition respective des molécules don't leurs particules intégrantes sont composées, *Annales de Chimie*, 90, 43–86, 1814.

3. C. Gerhardt, Recherches sur la Classification Chimique des Substances Organiques, *Comptes Rendus*, 15, 498–500, 1842.

4. The importance of the Karlsruhe conference in connection with the rationalization of atomic weights and the concept of the molecule is disputed by historian Alan Rocke, who claims that even without this meeting the changes would have occurred quite quickly. A. Rocke, *Chemical Atomism in the Nineteenth Century*, Ohio State Press, Columbus, 1984.

5. The question of whether Cannizzaro was committed to chemical or physical atomism is the subject of a study by Alan Chalmers. A. Chalmers, *The Scientist's Atom and the Philosopher's Stone*, Boston Studies in the Philosophy and History of Science (Book 279), Springer, Berlin, 2009. Chalmers believes that Cannizzaro would only be committed to the former.

6. For a detailed exposition of Cannizzaro's method, see J. Bradley, *Before and after Cannizzaro,* Whittles Publishing Services, North Humberside, UK, 1992.

7. S. Cannizzaro, *Il Nuovo Cimento*, 7, 321–366, 1858 (English translation Alembic Club Reprints, no. 18, Edinburgh, 1923), quoted from p. 11.

8. A. Naquet, *Principes de Chimie*, F. Savy, Paris, 1867.

9. The further inclusion of uranium in this group is incorrect in the light of modern knowledge.

10. The modern medium-long form of the periodic system separates out the transition metals, even though they show the same valence of 4, as in the case of zirconium and titanium.

11. I have argued elsewhere for a simultaneous discovery by these six researchers.

E.R. Scerri, The discovery of the periodic table as a case of simultaneous discovery. *Philosophical Transactions of the Royal Society A* 373: 20140172, 2015. http://dx.doi.org/10.1098/rsta.2014.0172

12. Inquirer, Numerical Relations of Equivalent Numbers, *Chemical News*, 10, 156, 1864; Studiosus, Numerical Relations of Equivalent Numbers, *Chemical News*, 10, 11, 1864; Studiosus, Numerical Relations of Equivalent Numbers, *Chemical News*, 10, 95, 1864.

13. P.J. Hartog, A First Foreshadowing of the Periodic Law, *Nature*, 41, 186–188, 1889; P.E. Lecoq De Boisbaudran, A. De Lapparent, A Reclamation of Priority on Behalf of M. De Chancourtois Referring to the Numerical Relations of the Atomic Weights, *Chemical News*, 63, 51–52, 1891.

14. A.E. Béguyer De Chancourtois, *Comptes Rendus de l'Académie des Sciences*, 54, 1862, 757, 840, 967.

15. Among the recipients of De Chancourtois's privately published system was Prince Napoleon.

16. A.E. Béguyer De Chancourtois, Mémoire sur un Classement naturel des Corps Simples ou Radicaux Apellé Vis Tellurique, *Comptes Rendus de l'Académie des Sciences*, 54, 757–761, 840–843, and 967–971, 1862.

17. P.J. Hartog, A First Foreshadowing of the Periodic Law, *Nature*, 41, 186–188, 1889; 186–188, quoted from p. 187.

18. J.A.R. Newlands, On the Construction of Tables Exhibiting the Composition and Mutual Reations of Organic Substances, *Journal of the Chemical Society*, 15, 1862, 36.

19. C.J. Giunta, J.A.R. Newlands, Classification of the Elements: Periodicity, but No System (1), *Bulletin for the History of Chemistry*, 24, 24–31, 1999.

20. As described below, Mendeleev repeated the first of Newlands's incorrect predictions concerning an element with an atomic weight in the region of about 170, along with making a number of other failed predictions of his own.

21. The chemical association of tellurium with sulfur and selenium and that of iodine with the halogen elements were well known on qualitative chemical grounds.

22. Newlands beat Odling by just four months in terms of publication dates: July 1864, as compared with October 1864 for Odling. I disagree with Carmen Giunta's denial of this anticipation and especially with the reasons that Giunta gives for taking this stance. C. Giunta, J.A.R. Newlands'; Classification of the Elements: Periodicity But No System, *Bulletin for the History of Chemistry*, 24, 24–31, 1999. A response to this article is E.R. Scerri, A Philosophical Commentary on Giunta's Critique of Newlands' Classification of the Elements, *Bulletin for the History of Chemistry*, 26, 124–129, 2001.

23. The qualitatively based systems of families of Hinrichs, Gmelin and Naquet, described earlier in this chapter, grouped lithium and sodium together.

24. A periodicity of 8 was correct for the chemistry known at the time. Today the periodicity is actually 9, counting from the first element up to and including the first analogous element (e.g., from lithium to sodium), as discussed in chapter 1.

25. J.A.R. Newlands, On the Law of Octaves, *Chemical News*, 12, 83, August 18, 1865, emphasis in the original.

26. Wendell H. Taylor, J.A.R. Newlands: A Pioneer in Atomic Numbers, *Journal of Chemical Education*, 26, 152–157, 1949.

27. W. Odling, On the Proportional Numbers of the Elements, *Quarterly Journal of Science*, 1, 642–648, October 1864, quoted from p. 648.

28. J.A.R. Newlands, On the Law of Octaves, *Chemical News*, 13, 130–130, 1866.

29. On the other hand, Newlands can be faulted for omitting gaps for as yet undiscovered elements in the manner that Mendeleev later did.

30. Here I am considering the distance between the number of successive similar elements, to be consistent with the Newlands quotation and not as in other parts of this book when considering one element up to and including its analogue.

31. J.A.R. Newlands, *On the Discovery of the Periodic System and on Relations among the Atomic Weights*, E&F.N., Spon London, 1884. Many copies of this book were published. The copy owned by the Science Museum in London is still displayed on open shelves and signed by Newlands himself.

32. W. Odling, On the Proportional Numbers of the Elements, *Quarterly Journal of Science*, 1, 642–648, October 1864, quoted from p. 642.

33. Ibid., quoted from p. 643.

34. W. Odling, On the Proportional Numbers of the Elements, *Quarterly Journal of Science*, 1, 642–648, 1864, quoted from p. 644.

35. Van Spronsen correctly praises Odling (pp. 112–116), in my view, for being the first to recognize this feature, although I differ somewhat regarding the details, as I argue in the main text.

36. Van Spronsen's claim (p. 113) that Odling had anticipated the separation of transition metals in the modern table would therefore need to be qualified somewhat.

37. Carl A. Zapffe, Hinrichs, Precursor of Mendeleev, *Isis*, 60, 461–476, 1969.

38. Ibid., p. 464.

39. In conversation with Bill Jensen, one very rainy evening in a Cincinnati restaurant, the author's car having broken down while en route to a conference in South Carolina.

40. H. Cassebaum, G. Kauffman, The Periodic System of the Chemical Elements: The Search for Its Discoverer, *Isis*, 62, 314–327, 1971.

41. The connection is altogether different from that postulated by Hinrichs, however.

42. Clearly, the correspondence with the astronomical distances is only approximate.

43. Isaac Newton is credited with first performing a similar experiment with sunlight, which he dispersed into its component colors, also by means of a glass prism.

44. It is said that Bunsen never once referred to the work of his former students, Mendeleev and Lothar Meyer, either in writings or in lectures. This was in spite of the fact that both of these former students acquired considerable fame for their respective systems of classifying the elements.

45. According to the atomic weights used by Hinrichs, calcium has a weight of 20 and barium a weight of 68.5.

46. One cannot exclude the possibility that he designed his system to fit the known facts.

47. The element didymium (Di) was included in many systems, including several of Mendeleev's tables. It eventually turned out to be a mixture of rare earth elements, praseodymium and neodymium.

48. In many ways, Newlands's earlier table, published in 1863, is more similar to that of Hinrichs in terms of groupings. Odling's table of 1864 also shows very similar groupings to Hinrichs's spiral table.

49. Admittedly, Newlands's grouping of all these elements makes sense in terms of secondary periodicity relationships as embodied in many short-form periodic tables. E.g., each of these elements shows a valence of 1.

50. G. Hinrichs, *The Elements of Chemistry and Mineralogy*, Davenport, Iowa; Day, Egbert, & Fidlar, 1871; G. Hinrichs, *The Principles of Chemistry and Molecular Mechanics*, Davenport, Iowa, Day, Egbert & Fidlar 1874.

51. G. Hinrichs, Natural Classification of the Elements, *The Pharmacist*, 2, 12, 1869.

52. K. Hentschel, Why Not One More Imponderable? John William Draper's Tithonic Rays, *Foundations of Chemistry*, 4, 5–59, 2002.

53. Part of the motivation for Cannizzaro's work on atomic weights lies with the earlier work of Avogadro, as mentioned above.

54. Lothar Meyer in his editorial on the papers of Cannizzaro in Oswald's *Klassiker der Exacten Wissenschaften*, vol. 30, Arbis eines Lehrganges der theoretischen Chemie, vorgetragen von Prof. S. Cannizzaro, Leipzig, 1891.

55. Thus, the compounds in any homologous series can be defined by a formula, and the molecular weight of successive members of such a series varies by a characteristic constant value. E.g., the compounds CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., are members of the alkane homologous series, and they all conform to the general formula of C_nH_{2n+2}. The radicals of this series, $CH_3 = 15$, $C_2H_5 = 29$, $C_3H_7 = 43$, and $C_4H_9 = 57$, increase in weight in intervals of 14, as do the compounds themselves.

56. Given the subsequent discovery of atomic substructure, this view may be considered one of the instances in which Lothar Meyer's thinking was more advanced than that of Mendeleev.

57. The modern atom may be said to be composite in the sense that it consists of smaller parts such as protons, neutrons, and electrons.

58. The term "horizontal relationship" may be a little ambiguous given that some tables show chemical groups vertically and others horizontally. I am using the term here in the sense mentioned in connection with Ernst Lenssen (see chapter 2) to mean relationships between elements that are not chemically analogous, or elements with steadily increasing atomic weights. These relationships appear horizontally as periods in the modern table and, indeed, in many but not all tables of the Lothar Meyer–Mendeleev period.

59. In the modern table, one sees an initial increase from valence 1 to valence 4 followed by a decrease down to 1 again, once the halogens are reached. Lothar Meyer's table differs from the modern one simply in that he chooses to begin with the modern group 14. In addition, the noble gases had not yet been discovered in 1864, and the modern group 13 had not yet been recognized as a separate group.

60. E.g., van Spronsen makes this criticism (p. 126).

61. The main reason for separating these elements must also be the valency relationships among them as well as more specific chemical similarities.

62. The original sense of the term "transition metal" referred to elements such as iron, cobalt, and nickel, which represented a "transition" between successive periods in the short-form table. In the modern sense, the term denotes a transition between the s- and p-blocks of the long-form tables, either medium-long or long forms. There are a total of 40 transition metals in the modern sense, up to and including element 112.

63. In his famous table of 1969, Mendeleev wrongly placed mercury with copper and silver; he misplaced lead with calcium, strontium, and barium; and he also misplaced thallium among the alkali metals. For a more detailed set of comparisons, see J. van Spronsen, *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969, pp. 127–131. The misplacement of mercury with silver is perhaps not altogether surprising given that *hydrargyrum*, the Latin name for mercury, means "liquid silver."

CHAPTER 4

MENDELEEV

Dmitri Ivanovich Mendeleev (figure 4.1) is the undisputed champion of the periodic system in at least two senses. First of all, he is by far the leading discoverer of the system. Although he was not the first to develop a periodic system, his version is the one that created the biggest impact on the scientific community at the time it was introduced and thereafter. His name is invariably and justifiably connected with the periodic system, to the same extent perhaps as Darwin's name is synonymous with the theory of evolution and Einstein's with the theory of relativity.

Although it may be possible to quibble about certain priority aspects of his contributions, there is no denying that Mendeleev was also the champion of the periodic system in the literal sense of propagating the system, defending its validity, and devoting time to its elaboration.[1] As discussed in chapter 3, there were others who produced significant work on the system, but many of them, such as Alexandre-Émile Béguyer De Chancourtois, William Odling, and Gustavus Hinrichs, moved on to other scientific endeavors. After publishing their initial ideas, these contributors devoted their attention to other fields and never seriously returned to the periodic system to examine its full consequences to the extent that Mendeleev did.

This is not to suggest that Mendeleev himself worked only on the periodic system. He is also known for many other scientific contributions, as well as for working in several applied fields, such as the Russian oil industry and as the director of the Russian institute for weights and measures. But the periodic system remained Mendeleev's pride and joy throughout his adult life. Even toward the end of his life he published an intriguing essay in which he returned to the periodic system and, among other speculations, attempted to place the physicist's ether within the periodic system as a chemical element.

Much has been written on Mendeleev, and it would be impossible to do justice to his contributions in the space of a few pages.[2] Here I concentrate, as in

FIGURE 4.1
Dimitri Ivanovich Mendeleev.
Photo and permission from
Emilio Segrè Collection.

other parts of this book, on the fundamental scientific and philosophical ideas that underpinned the evolution of the system.[3] An important part of this investigation consists of trying to understand Mendeleev's conception of the nature of chemical elements. This issue forms the basis of what is perhaps the most philosophical aspect of the periodic system and one that has been almost completely neglected by books and articles on Mendeleev and the periodic system generally.[4]

Early Life and Scientific Work

Mendeleev was born in 1834 in the Siberian city of Tobolsk. He was the last child in a family of 14 children. His father died when he was very young, and his mother, who was devoted to encouraging his scientific studies, died when Dmitri was about 15 years old. Before her death, she went to great lengths and sacrifices to enroll her son at the Main Pedagogical Institute of St. Petersburg, where he took classes in chemistry, biology, and physics, as well as pedagogy. The last of these in particular was to have a profound influence on his scientific work, since it was in the course of writing a textbook for the teaching of inorganic chemistry that Mendeleev was to develop his periodic system.

Mendeleev's early scientific work involved a detailed examination of the chemical properties as well as the specific volumes of many substances. In 1856, he spent some time working at Robert Bunsen's laboratory in Heidelberg, where he studied the behavior of gases and their deviations from the laws of perfect gases. In 1860 he was invited to attend the Karlsruhe conference, where he met the likes of

Jean-Baptiste André Dumas, Charles-Adolphe Wurtz, and Stanislao Cannizzaro. The following year he published a textbook of organic chemistry, which enjoyed considerable success in his native Russia and for which he was awarded the prestigious Demidov Prize.

It was not until 1865 that Mendeleev defended his doctoral thesis, which was based on his study of the interaction between alcohol and water. At about this time, having already written a book aimed at systematizing organic chemistry, he began to consider the possibility of producing a book that would likewise attempt to systematize inorganic chemistry. These efforts eventually resulted in his discovery of the periodic system, which is now virtually synonymous with his name.

Although it is clear that Mendeleev's periodic system was conceived while he was writing his textbook, *The Principles of Chemistry*, it is essential also to consider his shorter publications announcing the discovery of the periodic system, as well as earlier written evidence, in order to place this discovery in the wider context of his work. Many myths and legends have developed around the genesis of Mendeleev's periodic system, one of the most common being that he conceived of the idea in the course of a dream or that it occurred to him while playing a game of patience with cards marked with the symbols of the elements. In fact, the idea took many years to mature and may have begun to do so around the time of the Karlsruhe conference, as long as 10 years before the publication of his famous table of 1869.

At the end of 1868, Mendeleev had completed the first volume of his textbook on inorganic chemistry, in which he made a systematic examination of different kinds of elements and compounds and dealt with the most common elements, such as hydrogen, oxygen, and nitrogen. He initially grouped the elements according to the valences they displayed when combining with hydrogen. This offered at least some means of organization, but at this stage there was no sign of any overarching organizing principle or any system of classification. Mendeleev ended volume 1 with a survey of the halogens and began volume 2 with a survey of the alkali metals. He was then faced with the question of which elements to treat next. As legend has it, he solved the problem in the course of a single day, in which he declined to fulfill an obligation to inspect a nearby cheese factory, instead working furiously on his new element scheme.

The question of an organizing principle had to be faced, and unlike the precursors of the periodic system, with which he was familiar, Mendeleev did not embrace either the concept of triads or the existence of a primary substance. Mendeleev knew the work of the Belgian chemist Jean Servais Stas, for example, who had begun as an advocate of William Prout's hypothesis but, as noted in chapter 2, had become its strongest critic following a series of accurate atomic weight determinations he had himself undertaken. Mendeleev specifically refers to Stas in volume 1 of his book and expresses his distaste for Prout's hypothesis. Mendeleev's objection to a literal conception of triads is clear when he insists, also in volume 1, that rubidium, cesium, and thallium all belong to the alkali metals, along with the members of the original triad group, lithium, sodium, and potassium. Mendeleev is thus extending a group of elements previously thought to consist of just three elements to a group containing twice that number. In addition, he states that fluorine belongs to the halogens, thus extending the triad of chlorine, bromine, and iodine into a fourth member, a feat some others had resisted simply because it seemed to contradict the strict notion of a triad. Mendeleev thus explicitly freed himself from these pervasive general notions in order that his views might be judged on their own merit and so that the full originality of his work might be better appreciated.

On the other hand, although Mendeleev had grasped the importance of atomic weight early on, he had not fully embraced this means of characterizing the elements when he set out to write his textbook. The historian Donald Rawson, who has conducted a search of Mendeleev's views on atomic weights, finds that as early as 1855–1856, while an undergraduate at the Pedagogical Institute in St. Petersburg, Mendeleev was still using the atomic weights of Jacob Berzelius.[5] In his master's thesis, written shortly thereafter, Mendeleev had converted to the atomic weights of Charles Gerhardt, who had halved many of the values given by Berzelius. These values in turn also contained errors, including those for oxygen and carbon, which had been halved, thus resulting in the formula of water being considered H_2O_2 and that of benzene $C_{12}H_6$. Both of these are quite incorrect when compared with the modern formulas of H_2O and C_6H_6. Fortunately, Mendeleev readily abandoned Gerhardt's values when he attended the conference at Karlsruhe.[6]

Nevertheless, it took some further time before Mendeleev had fully converted to the atomic weights of Cannizzaro. In lecture notes written between the years 1864 and 1865, for example, Mendeleev listed 53 elements but still continued to use the more outdated equivalent weights for 13 of them. By 1868, when he began writing the second volume of his textbook, he was listing 22 elements, all of them given their new atomic weights according to Cannizzaro. Whether or not this is a coincidence, it implies that by the time Mendeleev had begun consciously to work on the classification of the elements, he had fully assimilated the use of the modern atomic weights, an approach that would prove to be so essential for his discovery.

It has been claimed that it was simply in seeking a quantitative justification for ordering the elements that Mendeleev arrived at the idea of using increasing atomic weights.[7] Although Mendeleev himself has written at some length on the genesis of his ideas, it is difficult to arrive at a clear and accurate picture of his motivations or even the course of the development of his thinking. For example, he steadfastly maintained in all subsequent writings that he did not see any of the systems developed by the five other discoverers of the periodic system, namely, De Chancourtois, Odling, Newlands, Hinrichs, and Lothar Meyer. This claim seems a little odd, given that he repeatedly acknowledged his debt to some earlier pioneers of the system, including Peter Kremers, Josiah Cooke, Max Pettenkofer, Jean-Baptiste Dumas, and Ernst Lenssen. Nor can it be supposed that this omission might have been due to isolation, since Russian chemistry, in particular, was rather advanced at this time, and Mendeleev had traveled in Europe and was well aware of the published literature in several languages.[8]

Also puzzling is the suggestion made by Mendeleev himself, as well as some later commentators, that it was the realization of the need to order the elements by atomic weight that was *the* bold and original step in the development of his system. Even if one grants that Mendeleev knew nothing of the work of the five other discoverers, surely the early precursors, whom Mendeleev so openly acknowledges, were already utilizing the concept of atomic weight in order to place the elements into some sort of order. One might rationalize this situation by recognizing that there is an important sense in which Mendeleev was indeed the first to recognize the *full* significance of the concept of atomic weight. We address this question after considering Mendeleev's actual discovery and the periodic tables he produced.

The Crucial Discovery

We now consider the crucial steps that led Mendeleev to begin comparing elements horizontally (in the sense of the modern periodic table) in terms of atomic weights.[9] There is a letter in the Mendeleev archives, dated February 17, 1869, which is also the date of the famous first table he produced.[10] This letter, from one Alexei Ivanovich Khodnev, secretary of the Free Economic Society in St. Petersburg, to Mendeleev concerns arrangements regarding the visit to a cheese factory where Mendeleev was due to conduct an inspection. On the back of the letter, Mendeleev has made a comparison of the atomic weights of the following elements:

Na	K	Rb	Cs
Be	Mg	Zn	Cd

This is where Mendeleev is possibly trying to decide which elements to discuss after the alkali metals in his book. It could either be zinc and cadmium or the alkaline earth elements, or perhaps even both together as shown in the fragment periodic table above. Indeed, this fragment may represent the first time that a horizontal comparison of the atomic weights of elements had been consciously carried out.[11]

Another early fragment periodic system that Mendeleev produced involves a comparison of three groups of elements:

F	Cl	Br	I				
Na	K	Rb	Cs			Cu	Ag
Mg	Ca	Sr	Ba	Zn	Cd		

On the same day, Mendeleev appears to have realized the need also to compare all the other groups of elements horizontally, thus allowing him to arrive at his first manuscript table, as shown in figure 4.2.

It would appear that, in the space of a single day, February 17, 1869, Mendeleev not only began to make horizontal comparisons but also produced the first version of a full periodic table that included most of the known elements. There should be no doubt, therefore, that a sudden decisive step *did* indeed occur, even though the background ideas may have been developing over a period of about 10 years.

We turn now to Mendeleev's announcement of his discovery. Having arrived at a consistent periodic system, Mendeleev had 200 copies of his table printed and sent them to chemists in Russia and the rest of Europe. Nicolai Alexandrovich Menshutkin communicated the initial discovery to the Russian Chemical Society on March 6. Later in the same month, it appeared in print (in Russian) in the first volume of the journal of the newly formed Russian Chemical Society.[12] The full article contained several periodic tables, and a shorter abstract was published in German a few weeks later.[13]

This first publication of Mendeleev's periodic system (figure 4.3) contains divisions into main and subgroups. The first column of elements, for example, shows valences of 1 but is divided into the alkali metals, such as lithium, sodium, and potassium, and the noble metals, including copper, silver, and gold. Significantly, there are several vacant spaces in the table, and Mendeleev proceeds even in this first publication to make several predictions, specifically anticipating "many yet unknown elements e.g. elements analogous to aluminium and silicon with atomic weights 65–75."

These predictions would become the elements scandium, gallium, and germanium, all of which were anticipated in the periodic tables published in this 1869 paper. Mendeleev made highly accurate entries for the expected atomic weights of two of these unknown elements in the form of "? = 68" and "? = 70" in the rows containing aluminum and silicon, respectively. (The atomic weights of these new elements turned out to be gallium = 69.2 and germanium = 72, respectively.) Moreover, his "attempt at a system" of 1869 contains an entry "? = 45," which turned out to correspond to scandium with an atomic weight of 44.6, although it has been the subject of some debate whether Mendeleev's early prediction of this element can be strictly identified with scandium.

Not only did Mendeleev predict the atomic weights of his famous three new elements as early as 1869, but he also made predictions of some of their other properties. In a talk to a Moscow Congress in that same year, he suggested that two elements missing from the system would show resemblances to aluminum and silicon and would have atomic volumes of 10 or 15 and specific gravities of about 6. In the following year, 1870, Mendeleev listed the expected atomic volumes of the elements that would become known as scandium, gallium, and germanium as 15, 11.5, and 13, respectively.[14]

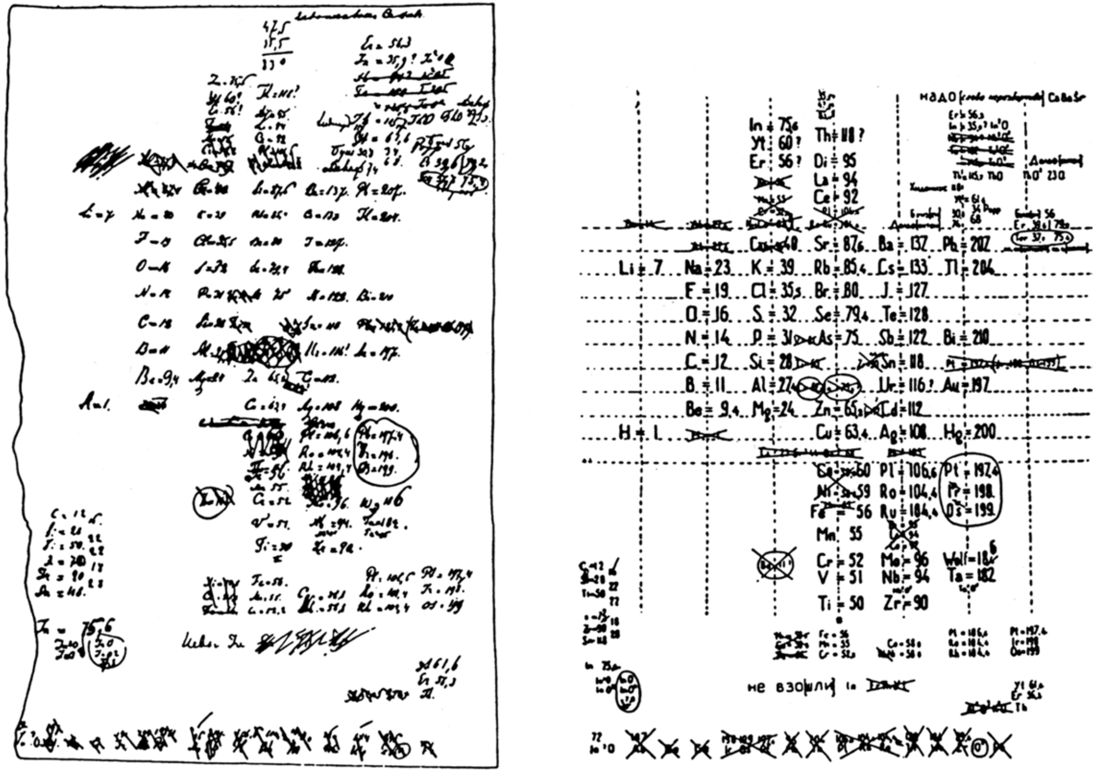
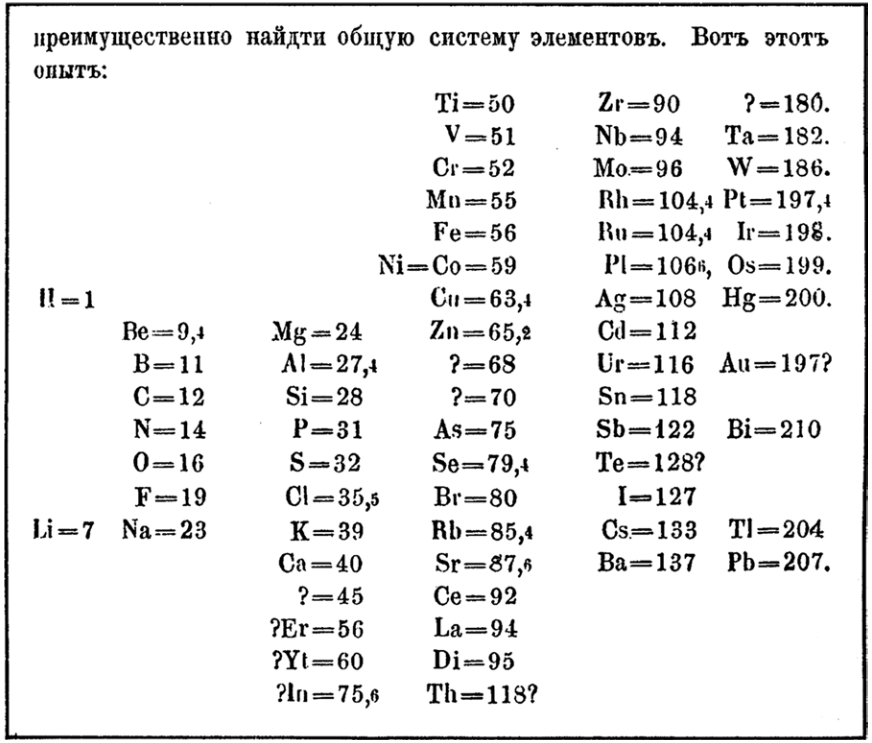


FIGURE 4.2 Mendeleev's first periodic system, in draft form: photocopy of original manuscript (left), and clarified version (right). D.I. Mendeleev, *Periodicheskii Zakon: Klassiki Nauki*, B.M. Kedrov (ed.), Izdatel'stvo Akademii nauk Soyuz sovietskikh sotsial'sticheskikh respublik , Moscow, 1958. Reproduced from Van Spronsen by permission of publisher.



преимущественно найдти общую систему элементовъ. Вотъ этотъ опытъ:

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6,	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

FIGURE 4.3 Mendeleev's first published periodic system, of 1869. D.I. Mendeleev, Sootnoshenie svoistv s atomnym vesom elementov, *Zhurnal Russkeo Fiziko-Khimicheskogo Obshchestva,* 1, 60–77, 1869, 1, 60–77, 1869, p. 70.

Another evident feature of this system is the reversal of the elements tellurium and iodine, although, as mentioned in chapter 3, this step had already been taken by Odling and Lothar Meyer, regardless of whether or not Mendeleev might have been aware of this fact. In putting tellurium before iodine, Mendeleev was departing from his general approach of ordering the elements by atomic weight. As mentioned in chapter 3, tellurium has a higher atomic weight than iodine, and yet in terms of its valence, tellurium should occur before iodine in the ordering of the elements. But apart from this particular case, Mendeleev did not maintain the use of valence as a criterion for classification as had Lothar Meyer, for example, because many elements show variable valences and because of his philosophical preference for concentrating on elements as basic substances rather than elements with manifest chemical properties, as discussed below. Some aspects of this attitude are revealed in his writing:

> Not being susceptible to exact measurements, the above mentioned chemical properties can hardly serve to generalize chemical knowledge:They alone cannot serve as a basis for chemical considerations. However, the properties should not be altogether neglected as they explain a great number of chemical phenomena.[15]

Mendeleev consequently put more faith in his newly discovered criterion for ordering the elements according to atomic weight.

Some idea of the sophistication of Mendeleev's first article, as well as the German abstract, can be seen from the list of eight points with which he ends these publications:

1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.
2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium), or which increase regularly (e.g., potassium, rubidium, caesium).
3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds to their so-called *valences* as well as, to some extent, to their distinctive chemical properties—as is apparent among other series—in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.
4. The elements which are most widely diffused have *small* atomic weights.
5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.
6. We must expect the discovery of many yet *unknown* elements, for example, elements analogous to aluminium and silicon, whose atomic weight should be between 65 and 71.
7. The atomic weight of an element may sometimes be amended by a knowledge of those of contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.
8. Certain characteristic properties of the elements can be foretold from their atomic weights. (All italics are in the original.)

The manner and clarity with which Mendeleev expresses these points are rather striking in that he makes quite explicit what many of the codiscoverers only hinted at. It also shows us clearly the depth of Mendeleev's chemical knowledge, a theme that will be further explored in chapter 5, which considers the manner in which he placed particular elements into his system.

In the same year of 1869, Mendeleev also published a lesser known system in which the separation into main and subgroups does not feature in any way whatsoever (table 4.1). For example, the elements lithium, sodium, potassium, copper, rubidium, silver, cesium, and thallium are all just grouped together as the first horizontal row of the table. This publication, his second major one on the periodic system, appeared as a report of a meeting of the Russian chemists and is dated August 23, 1869.

In his third article, published in 1870, Mendeleev was already considering the possibility that his system had been completed, at least in principle.[16] Among the features displayed in this article are the relocation of uranium from the boron group to the chromium group and a corresponding change in its atomic weight from 116 to 240.[17] In addition, the atomic weight of indium is changed from 75 to 113, which allows Mendeleev to locate the element in the boron group rather than merely leaving it ungrouped at the very bottom of his table as he did in 1869.[18] Other changes included cerium being given a new atomic weight and its being moved. Thallium is also given a new atomic weight. With the exception of the placement of uranium, these changes are essentially correct from a modern perspective.[19]

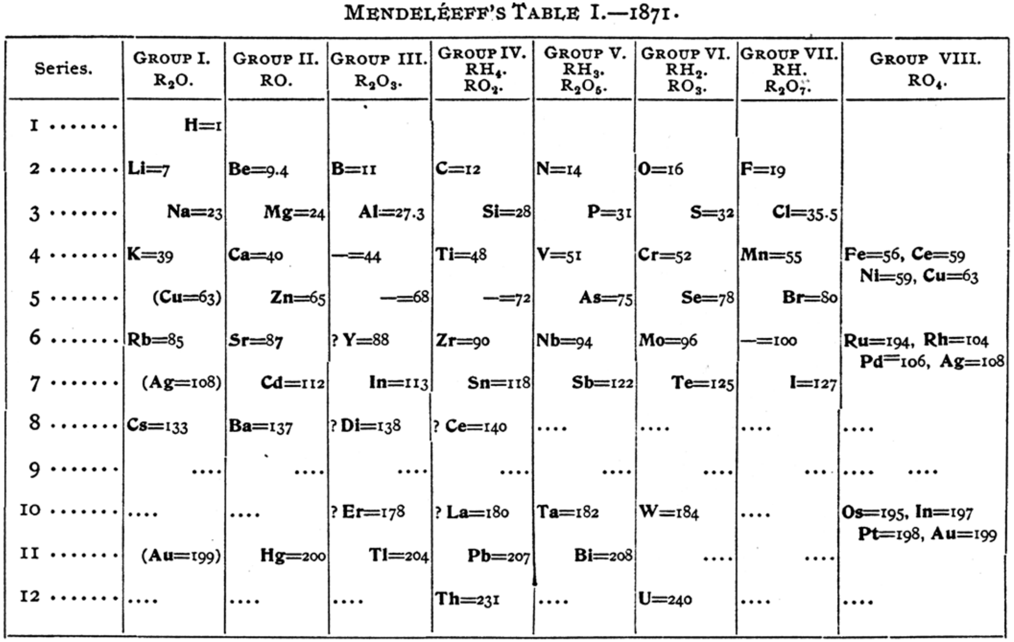
In 1871, Mendeleev published an extensive 96-page article in German containing tables in which he grouped elements vertically (figure 4.4) as well as horizontally. It was in this article that Mendeleev spelled out his detailed predictions that, when later confirmed, were to make him famous.

In all, Mendeleev published approximately 30 periodic tables and designed a further 30 tables which remained in manuscript form. These included horizontal

TABLE 4.1
Mendeleev's spiral table of 1869.

Li	Na	K	Cu	Rb	Ag	Cs	—	Tl
7	23	39	63.4	85.4	108	133	—	204
Be	Mg	Ca	Zn	Sr	Cd	Ba	—	Pb
Be	Al	—	—	—	Ur	—	—	Bi?
C	Si	Ti	—	Zr	Sn	—	—	—
N	P	V	As	Nb	Sb	—	Ta	—
O	Si	—	Se	—	Te	—	W	—
F	Cl	—	Br	—	J	—	—	—
19	35.5	58	80	100	127	160	190	220

Redrawn from D.I. Mendeleev, *Zhurnal Russkeo Fiziko-Khimicheskoe Obshchestvo*, 1, 60–77, 1869. The table is located in a footnote, which begins on p. 69 and ends on p.70.



MENDELÉEFF'S TABLE I.—1871.

Series.	GROUP I. R_2O.	GROUP II. RO.	GROUP III. R_2O_3.	GROUP IV. RH_4. RO_2.	GROUP V. RH_3. R_2O_5.	GROUP VI. RH_2. RO_3.	GROUP VII. RH. R_2O_7.	GROUP VIII. RO_4.
1 ·······	**H**=1							
2 ·······	**Li**=7	**Be**=9.4	**B**=11	**C**=12	**N**=14	**O**=16	**F**=19	
3 ·······	**Na**=23	**Mg**=24	**Al**=27.3	**Si**=28	**P**=31	**S**=32	**Cl**=35.5	
4 ·······	**K**=39	**Ca**=40	—=44	**Ti**=48	**V**=51	**Cr**=52	**Mn**=55	**Fe**=56, **Ce**=59 **Ni**=59, **Cu**=63
5 ·······	(**Cu**=63)	**Zn**=65	—=68	—=72	**As**=75	**Se**=78	**Br**=80	
6 ·······	**Rb**=85	**Sr**=87	? **Y**=88	**Zr**=90	**Nb**=94	**Mo**=96	—=100	**Ru**=194, **Rh**=104 **Pd**=106, **Ag**=108
7 ·······	(**Ag**=108)	**Cd**=112	**In**=113	**Sn**=118	**Sb**=122	**Te**=125	**I**=127	
8 ·······	**Cs**=133	**Ba**=137	? **Di**=138	? **Ce**=140	....	....	....	....
9 ·······	....	....	....	....	....	....	....	....
10 ·······	....	....	? **Er**=178	? **La**=180	**Ta**=182	**W**=184	....	**Os**=195, **In**=197 **Pt**=198, **Au**=199
11 ·······	(**Au**=199)	**Hg**=200	**Tl**=204	**Pb**=207	**Bi**=208	....	....	
12 ·······	....	....	....	**Th**=231	....	**U**=240	....	....

FIGURE 4.4 Mendeleev's table of 1871. Estestvennaya sistema elementov i primenie ee k ukazaniyu svoistv neotkrytykh elementov, *Zhurnal Russkeo Fiziko-Khimicheskogo Obshchestva*, 3, 25–56, 1871.

tables, vertical tables, helical tables, and even long-form tables. The last-named are popularly thought to have originated following the introduction of quantum mechanics into chemistry, and yet an example of such a table, by Mendeleev from 1879, is shown in table 4.2.

The Nature of the Elements

This brief summary of the progression of Mendeleev's tables brings us to what I believe is the core philosophical idea of the periodic system. It is an idea so philosophically rich that it has hardly begun to be explored by modern scholars. It may perhaps be the key to many previously unanswered questions regarding the periodic system, such as why it was Mendeleev, above all others, who was prepared to venture forth to make bold predictions, while others tended to be "intimidated" by the prevailing empirical data on the elements.

In the course of developing his system, Mendeleev acknowledged the question of how the elements manage to survive intact in any compound in which they might find themselves. One may consider the common example of sodium chloride, and the fact that the gray and poisonous metal sodium and the green poisonous gas chlorine apparently are nowhere to be found after their chemical combination to form the white crystalline compound sodium chloride.

In order to answer this question, Mendeleev appealed to a long-standing notion in chemical philosophy dating back to Aristotle. For Aristotle, the elements

TABLE 4.2
Mendeleev's long-form periodic table of 1879.

										even elements						
										I	II	III	IV	V	VI	VII
										H						
										LI	Be	B	C	N	O	F
										Na						
event elements										odd elements						
I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII
										—	—	—	—	—	—	—
—	—	—	—	—	—	—				—	Mg	Al	Si	P	S	Cl
K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	—	—	—
Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Er	Di?	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—

Redrawn from D.I. Mendeleev, *Chemical News*, 40, 231–232, 231.

themselves were to be regarded as abstract, even though they gave rise to all the physical variety that is observed. The four elements (fire, earth, water, air) were considered as property bearers responsible for the tangible features of substances, although they were themselves unobservable.[20] The elements were immaterial qualities impressed on an otherwise undifferentiated primordial matter and were present in all substances. Thus, the proportion of the four elements present within a specific substance governed its properties.

This view was challenged, among others, by Antoine Lavoisier during the course of the chemical revolution in the eighteenth century, giving rise to a "new chemistry," which drew upon the Aristotelian tradition while making important modifications. The new chemistry introduced the concepts of *simple substance* and *material ingredient* of substances. A simple substance was one that could not be decomposed by any known means. The inclusion of the word "known" here is very important, since the scheme proposed that simple substances were to be regarded as such only provisionally, since they might lose this status following future refinements in analytical techniques. A major departure from Aristotle's scheme was that not all substances had to contain every one of these simple substances. There was no longer thought to be one undifferentiated primordial matter but instead a number of elementary constituents, or simple substances, now possessed of observable properties.

As a result of Lavoisier's work, it became a relatively simple experimental question to determine which substances were simple and which were not, and as mentioned in chapter 1, Lavoisier and his contemporaries created a list of the 37 simple substances known at the time. One consequence of Lavoisier's scheme, however, was that abstract elements did not necessarily correspond to particular known simple substances. Since it was possible that what was regarded as a simple substance at a particular stage in history might turn out to be decomposable, one would need to have perfect confidence in one's analytical techniques to be certain of the correspondence between a simple substance and an abstract element. To his credit, Lavoisier only provisionally identified with abstract elements those simple substances that had been isolated. Such caution began to fade toward the end of the nineteenth century, however, to the extent that simple substances began to be regarded as the only form of an element, and the abstract counterpart to each simple substance was largely forgotten.

And yet the abstract/metaphysical aspect of elements was not completely neglected, continuing to serve an explanatory function in nineteenth-century chemistry, though not necessarily as a microscopic explanation.[21] A chemist could be skeptical of atomistic explanations, as Mendeleev and many others were in the nineteenth century, and yet could readily accept a metaphysical explanation for chemical phenomena. In fact, one benefit of regarding the elements as having a metaphysical status is that it provides a way out of the apparent paradox, which Mendeleev was attempting to address, concerning the nature of elements when combined together in compounds. Again, with sodium chloride, one can ask in what sense the elements sodium and chlorine continue to exist in common salt. Clearly, the elements themselves, in the modern sense of the word, do not appear to survive or else they would be detectable, and one would have a mixture of sodium and chlorine that could show the properties of both of these elements. The response available from the nineteenth-century element scheme is that simple substances do *not* survive in the compound, only abstract elements do.[22]

According to the nineteenth-century scheme, these abstract elements were believed to be permanent and responsible for the observable properties of simple bodies and compounds.[23] However, in a major departure from the Aristotelian view, the abstract elements were also regarded as being "material ingredients" of simple bodies and compounds. This concept of material ingredient thus served to link the metaphysical world of abstract elements and the observable, material realm of simple substances. For example, the stoichiometric relationships observed in chemical changes were explained in terms of amounts of abstract elements present in the reacting substances through the agency of the material ingredient.

There are thus three important concepts regarding elements carried over into the nineteenth century. First, the abstract element is a property bearer and owes its heritage to the Aristotelian element scheme.[24] Second, in addition to being a property bearer, the abstract element is an indestructible material ingredient of substances, behaving according to Lavoisier's law of the conservation of matter. The third concept is that an abstract element is unobservable, whereas simple substances such as sodium, chlorine, and oxygen can be observed. It should be noted that in contemporary chemistry only the last notion seems to be retained, in that the term "element" is limited to what a nineteenth-century chemist would have called a simple substance.[25]

The culmination of the nineteenth-century element scheme was reached with the discovery of the periodic system and the work of Mendeleev, who begins his book by paying tribute to Lavoisier.[26] More than any other discoverer, Mendeleev was concerned with the philosophical status of the elements. It is an important and rather overlooked aspect of Mendeleev's approach to the periodic system that he distinguished carefully between what he terms "simple substance" and "element."[27] Unlike the periodic law itself, which seemed to have achieved full maturity only when Mendeleev had reached the end of the first volume,[28] the discussion of simple substance and abstract element occurs right at the beginning of the first volume and is revisited on several occasions in the course of the book:[29]

> It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself.[30]

For Mendeleev, the element was an entity, which was essentially unobservable but formed the inner essence of simple bodies. Whereas a particular "element" was to be regarded as unchanging, its corresponding simple body aspect could take many forms, such as charcoal, diamond, and graphite, in the case of carbon. In this respect, Mendeleev may be thought of as upholding the ancient philosophical tradition regarding the nature of elements as bearers of properties.[31] Mendeleev's genius now lay in recognizing that just as it was the "element" that survived intact in the course of compound formation, so atomic weight was the only quantity that survived in terms of measurable attributes. He therefore took the step of associating these two features together. An element (basic substance) was to be characterized by its atomic weight. In a sense, an abstract element had acquired a single measurable attribute that would remain unchanged in all its chemical combinations. Here is a profound justification for using atomic weight as the basis for the classification of the elements, quite unlike anything produced by other discoverers or precursors of the periodic system. How else is one to make sense of Mendeleev's otherwise rather naive-sounding claim that he had realized the need to order the elements according to atomic weight, given that others had done so before him? The point is that he was providing a detailed account of why this was the correct approach to take.[32]

Mendeleev's periodic system was presented at the end of the first of the two volumes of his textbook on inorganic chemistry. His book was first published in Russian but then was eventually translated into English, French, and German. The first English edition, a translation of the fifth Russian edition, appeared in 1891, that is, about 20 years after the first Russian edition.[33] Of course, most serious chemists in Europe first heard about Mendeleev's work through published articles rather than his book. Although Mendeleev never fully revised his textbook for its successive editions, the gradual evolution of his thoughts on atomic weight and the ordering of the elements can be traced through the voluminous footnotes that were added to it at various stages.

The Japanese historian Masanori Kaji conducted a detailed survey of all eight successive editions of Mendeleev's book in the original Russian.[34] By studying the first Russian edition, which was never translated, Kaji argued that Mendeleev began his textbook by using the concept of valency as a means of ordering the elements. This is clearly revealed in the fact that Mendeleev considers the following elements in order: hydrogen, oxygen, nitrogen, and carbon, whose valences are 1, 2, 3, and 4, respectively.

Then Mendeleev turns to the halogens, beginning again with the valence of 1.[35] These are followed by a consideration of the alkali metals, also of valence 1, and then the divalent alkaline earths. As mentioned above, it was while making the transition between the alkali metals and the alkaline earths that Mendeleev appears to have made the crucial discovery that allowed him to produce the periodic system. Essentially, he realized that the key to classifying the elements was not valency but atomic weight. Now, of course, many previous chemists had been aware of this fact, either implicitly or explicitly, in proposing tables based on triads or differences between atomic weights of the elements. Nevertheless, Mendeleev added an important ingredient in realizing the possibility of comparing chemically dissimilar elements or, as one might say with hindsight, comparing elements placed horizontally in the present form of the periodic table.[36] As Mendeleev states:

> The purpose of my paper would be entirely attained if I succeed in turning the attention of investigators to the very relationships in the size of the atomic weights of nonsimilar elements, which have, as far as I know, been almost entirely neglected until now.[37]

Kaji claims that at least three noted authorities on the periodic system[38] have been mistaken in proposing that Mendeleev deliberately refrained from revising successive editions of his textbook in order to show his readers how his ideas evolved over time. Some of these authors have even proposed that we should ignore what Mendeleev himself says about the genesis of his periodic system and that we should trace the development of his ideas in the textbook itself, in all its permutations. But this suggestion is rather unconvincing since Mendeleev may have simply been too busy to undertake a thorough revision of the textbook, especially given his many and widely scattered interests. Perhaps we should also be less inclined to dismiss Mendeleev's own accounts of how he arrived at the periodic system. Clearly, this topic has not yet been sufficiently researched by Mendeleev scholars.

What still remains unexplained is why Mendeleev did not completely revise the first part of the book to comply with the way the elements were arranged in his newly discovered periodic system. In the third edition, the second of the two volumes was rearranged so that the discussion of the elements would follow the sequence in which they appear in the periodic system. There has been some debate as to whether this should be considered a major reorganization, but clearly the third edition bears some signs of the discovery of the periodic system. Indeed, it would also have been rather surprising if later editions of Mendeleev's book bore absolutely no benefits from his discovery of the periodic system.

The fifth edition of *The Principles of Chemistry*, which appeared in 1889, is of particular importance to Western scholars since it was the first one to be translated into English, French, and German. It contains some changes from the previous editions, but still, these are not substantial enough to constitute a major revision. Three further editions, the sixth, seventh, and eighth, were published, and a few changes were made to these editions. For example, in the seventh edition, published in 1903, the recently discovered element argon was incorporated into the periodic system but discussed in the course of the chapter on nitrogen and the air, presumably because argon was first isolated in small amounts from samples of nitrogen. Mendeleev also mentions the newly isolated element radium, while denying any possibility of transmutation of elements and while attempting to explain the phenomenon of radioactivity by appealing to the ether. Moreover, Mendeleev, who had struggled with the placement of the rare earth elements for an extended period of time, finally relinquished all attempts to do so to the Czech chemist

Bohuslav Brauner, who contributed the chapter on the rare earths in the last edition of Mendeleev's book. In this, the eighth and final edition to be published during Mendeleev's lifetime, all footnotes are finally separated from the main text and placed in the second half of the book.

Making Predictions

Lothar Meyer and others preceded Mendeleev in predicting the existence of unknown elements, but it is beyond dispute that Mendeleev made far more extensive predictions than any of the codiscoverers of the periodic system. Not only did he successfully predict new elements, but he also corrected the atomic weights of a number of known elements, as well as correctly reversing the positions of the elements tellurium and iodine. Why was it Mendeleev who was able to make such striking predictions and not Lothar Meyer or others? Is it simply that the others lacked the courage to do so, as many historians of science state?[39] I want to suggest that Mendeleev's advantage lay in his philosophical approach to chemistry, for it allowed him to arrive at insights his less philosophically minded contemporaries could not have entertained.

Mendeleev realized that abstract elements were to be regarded as more fundamental than simple substances. The explanation of why "elements" persist in their compounds was to be found in abstract elements and not simple substances, and as a consequence, if the periodic system were to be of fundamental importance, it would primarily have to classify the abstract elements. The predictions Mendeleev made were thus conceived of with the abstract elements in mind. If the available observational data on simple substances pointed in a certain direction, these features could be partly overlooked in the belief that the properties of the more fundamental abstract elements might be different from what had been observed up to that point in the form of a particular "simple substance." Of course, any prediction must eventually be realized by the isolation of a corresponding simple substance, precisely because "elements," in the more subtle sense of the term, are beyond observation. This requirement presented no problem to Mendeleev, however, for he believed that elements possess one significant and measurable attribute, namely, their atomic weight. In other words, his predictions of abstract elements could be identified empirically through their material ingredient in the form of their atomic weights.[40] As noted above, Mendeleev believed that atomic weight was the one property that does not change when an element combines to form compounds, whereas all the other properties of simple substances seem to be radically altered upon chemical combination.

Because he was attempting to classify abstract elements, not simple substances, Mendeleev was not misled by nonessential chemical properties. For example, the elements in the halogen group (fluorine, chlorine, bromine, and iodine) appear to be rather different from each other when one focuses on them as isolable simple substances, since they consist of two gases, a liquid and a solid, respectively. The similarities among the members of the group are more noticeable when considering the compounds each one forms with sodium, for example, all of which are crystalline white powders. The point is that in these compounds, fluorine, chlorine, bromine, and iodine, are present not as simple substances but in a latent, or essential, form as basic substances.[41]

Thus, his view of the elements allowed Mendeleev to maintain the validity of the periodic law even in instances where observational evidence seemed to point against it.[42] Such boldness may have resulted from a deeply held belief that the periodic law applied to the abstract elements as basic substances and that this law was as fundamental and equal in status to Newton's laws of mechanics. Had he been more of a positivist, Mendeleev might easily have lost sight of the importance of the periodic law and might have harbored doubts about some of his predictions.

On one of the few occasions that Mendeleev allowed himself to express his philosophical views, he wrote of the relationship between "matter, force, and spirit." He claimed that contemporary philosophical problems stemmed from a tendency to search for one unifying principle, while he favored three basic components of nature: matter (substance), force (energy), and spirit (soul). Everything was composed of these three components, and no one category could be reduced to any of the others. According to Michael Gordin, Mendeleev's use of "spirit" amounts to the modern notion of essentialism, or that which is irreducibly peculiar to the object in question. Gordin also adds that Mendeleev's position is clearly metaphysical, thus removing him from the "companionship of positivists" and thus consistent with the position adopted by the present author.[43]

Mendeleev as Reductionist?

Whereas Mendeleev was clearly ahead of his competitors when it came to the prediction of elements, he does not seem to have fared so well with regard to his views on the reduction of chemistry. Textbooks often wax lyrical about the manner in which it is now believed the periodic system is dependent upon the electronic structure of atoms, whereas Mendeleev was concerned almost exclusively with chemical properties. Sometimes the fact that Mendeleev could construct the periodic system merely from considering chemical properties is marveled at in a rather patronizing fashion. Textbook accounts typically express surprise that he was able to deduce the periodic system from such apparently crude data. But as I have argued here, Mendeleev did not primarily classify the elements according to chemical properties.

More specifically, Mendeleev's denial of the reduction of chemistry has generally been held to be mistaken, especially in view of the subsequent discoveries of radioactivity and the structure of the atom. That historians of chemistry have reached such a conclusion is not at all surprising, especially given some of Mendeleev's own pronouncements on the subject. In his Faraday lecture, delivered at the Royal Institution in London, he said:

> [T]he periodic law . . . has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; it has no historical connection with that relic of the torments of classical thought.[44]

Here Mendeleev is expressing his opposition to one kind of reductionism, namely, the reduction of all matter to one form of matter, as in Prout's hypothesis.

In other instances, Mendeleev appears to express views on an altogether different form of reductionism. This is the view that elements, or atoms of the elements, in modern terms, can be broken down:

> By many methods founded both on experiment and theory, has it been tried to prove the compound nature of the elements. All labour in this direction has as yet been in vain, and the assurance that elementary matter is not so homogeneous (single) as the mind would desire in its first transport of rapid generalization is strengthened from year to year.[45]

Not only did Mendeleev deny that all elements could be reduced to one form of matter, namely, hydrogen, as in Prout's view, but he also denied that the various elements would be found to be composed of more universal building blocks. But modern physics has revealed that the atoms of the elements do indeed have a "compound" nature, since they are composed of protons, neutrons, and electrons. Moreover, the nucleus of the atom, which in simple terms contains just protons and neutrons, has been found to give rise to a staggering 300 or so subnuclear particles. Needless to say, Mendeleev could not have known of these developments.

In emphasizing atomic weight as the key criterion for ordering the elements, Mendeleev also relegates chemical properties to a certain extent. Depending on how much importance one is prepared to place on this feature, Mendeleev might be viewed as a direct precursor to the modern reductionist tendency in chemistry. This is the tendency that reached greater heights in the 1920s and 1930s via the implementation of quantum mechanics, which continues to this day. Mendeleev's emphasis on atomic weight, above all else, might thus be regarded as a classic example of reductionism that places him in the vanguard of the twentieth-century approach to science rather than at the tail end of the classical chemical tradition, where some authors believe that he belongs.

There are many kinds of reductionism. Mendeleev may not have believed in the unity of all matter, but he was an influential proponent of the reduction of chemistry to physics in another sense, that is, in attaching great importance to physical data concerning the elements and especially their atomic weights. Indeed, it was the essence of his achievement that he elevated the ordering of the elements by atomic weight to the status of a law, protecting his emerging periodic system from the uncertainties of the chemical knowledge of his time. At the same time, Mendeleev's understanding of the individual chemical natures of the elements, and their compounds, was profound. This understanding gave him an intuitive sense of how the elements should be grouped. In fact, it can be argued that, although his views on the compound nature of elements and their atoms would turn out to be incorrect, Mendeleev would not have needed to change his position on the basis of current knowledge. As Fritz Paneth suggests,

> Yet I believe that something very essential in his [Mendeleev's] fundamental philosophical tenets would have remained untouched by the progress in physics and could be successfully defended even today; and it is just these "philosophical principles of our science" which he regarded as the main substance of his textbook.[46]

This resolution can be appreciated by realizing that Mendeleev adopted an intermediate position between realism and reduction to physics. Even though physics has revealed that atoms of the elements can be decomposed, it is still the case that chemists can continue to ignore this deeper structure for many chemical purposes.[47] This is the essence of Mendeleev's intermediate position, whereby it is more useful to regard the elements as having distinct identities and yet as also being decomposable into the same fundamental particles such as protons and electrons, in modern terms. It is the view that every science can decide for itself the level at which it should operate and that the deepest foundations are by no means always the best for every purpose.

As the French philosopher Gaston Bachelard, who began his career as a physical chemist, has written:

> La pensée du chimiste nous parait osciller entre le pluralisme d'une part et la reduction du pluralisme d'autre part. (The chemist's thinking seems to oscillate between pluralism on one hand, and the reduction of pluralism on the other hand.)[48]

Mendeleev, the creator of the periodic system of the elements, drew the philosophical distinction between basic substances (abstract elements) and simple substances. He cannot, therefore, be regarded as a naive realist. However, having arrived at the periodic classification by giving emphasis to abstract elements, he resisted the prevalent reductionist tendency of supposing the existence of a primary matter. He considered the elements as distinct individuals and adopted an intermediate position between realism and reduction.[49] This may be Mendeleev's true legacy. Perhaps it can provide the foundation of a genuine "philosophy of chemistry," which is as relevant today as ever, though it has been largely neglected.[50]

Notes

1. In an earlier article in *Scientific American*, I implied that Mendeleev had spent the remainder of his life in elaborating the periodic system. This view has now been corrected by Michael Gordin. See M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004.

2. M.D. Gordin, The Organic Roots of Mendeleev's Periodic Law. *Historical Studies in the Physical and Biological Sciences* 32(1): 263–290, 2002; M. Gordin, *A Well-Ordered Thing*; N.M. Brookes, Dimitrii Mendeleev's *Principles of Chemistry and the Periodic Law of the Elements,*

in B. Bensaude-Vincent, A. Lundgren (eds.), *Communicating Chemistry: Textbooks and Their Audiences 1789–1939*, Science History Publications, Canton, MA, 2000, pp. 295–309.

3. Not being a reader of the Russian language, I have not been able to consult the primary literature, as have contemporary Mendeleev scholars.

4. The question of the nature of elements is mentioned in Jan van Spronsen's book *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969. One of the few articles to examine the issue is a two-part paper by F.A. Paneth, The Epistemological Status of the Chemical Concept of Element, *British Journal for the Philosophy of Science*, 13, 1–14, 144–160, 1962. Another analysis has been given in an unpublished PhD thesis written in French by Bernadette Bensaude-Vincent, *Les Pièges de l'Elémentaire*, Université de Paris, 1981. (I am grateful to the author for sending me a copy.)

5. D.C. Rawson, The Process of Discovery: Mendeleev and the Periodic Law, *Annals of Science*, 31, 181–193, 1974.

6. Rawson refers to a letter from Mendeleev to his mentor, Aleksandr Voskresenskii, in which he describes how he is impressed by Cannizzaro's system, which is based on Amedeo Avogadro's hypothesis.

7. The Russian expert on the periodic table, Bonifatii Kedrov, has made this claim.

8. It may even be that Mendeleev consciously avoided mentioning his immediate precursors and competitors, although I have no evidence to support this notion.

9. For a more detailed account, see M. Gordin's book, *A Well-Ordered Thing*, Basic Books, New York, 2004.

10. At this date, Russia was still using the Julian calendar of the Roman Empire. Most other European countries had switched to the Gregorian or reformed calendar, according to which the date would have been March 1.

11. As mentioned in chapter 2, Kremers also did something of this kind, but it appears that the comparison was not made consciously.

12. D.I. Mendeleev, Sootnoshenie svoistv s atomnym vesom elementov, *Zhurnal Russkeo Fiziko-Khimicheskoe Obshchestvo*, 1, 60–77, 1869.

13. The German abstract of Mendeleev's famous first paper on the periodic system appeared in the *Journal für Praktische Chemie*, 1, 251, 1869, and a longer article summarizing Mendeleev's first article appeared in *Berichte der deutschen chemischen Gesellschaft*, 2, 553, 1869.

14. Mendeleev, Manuscript Table 19 (M13), dating from summer–early fall of 1870 (the numbering denotes the 13th manuscript table and the 19th table in the overall sequence of 65 tables of all forms).

15. D. Mendeleev, The Periodic Law of the Chemical Elements, *Chemical News*, 40, 243–244, November 21, 1879, quoted from p. 243. Mendeleev specifically mentions combination with oxygen and hydrogen. The quote appears in one of 18 sections of a serialization that appeared in *Chemical News*, 1879, 40, 231–232, 243–244, 255–256, 267–268, 279–280, 291–292, 303–304, Ibid., 1880, 41, 2–3, 27–28, 39–40, 49–50, 61–62, 71–72, 83–84, 93–94, 106–108, 113–114, 125–126.

16. D.I. Mendeleev, Über die Stellung des Ceriums in System der Elemente, *Bulletin of the Academy of Imperial Science (St. Petersburg)*, 16, 45–51, 1870.

17. The basis on which Mendeleev carried out this change is analyzed in chapter 5.

18. Lothar Meyer had also moved indium in this way.

19. Mendeleev's grounds for making these changes varied considerably. E.g., his moving the element uranium from the boron group to the chromium group is discussed in detail in chapter 5.

20. E.R. Scerri, Realism, Reduction and the Intermediate Position, in N. Bhushan, S. Rosenfeld (eds.), *Of Minds and Molecules*, Oxford University Press, New York, 2000, pp. 51–72.

21. In using the word "metaphysical," I am following the work of Fritz Paneth on this question. Some contemporary philosophers of chemistry, e.g., Paul Needham and Robin Hendry, deny any metaphysical notion when discussing the question of basic substances.

22. The more prosaic explanation given in contemporary chemistry is that what survives of each of the elements is the number of protons, in other words, the nuclear charge of the atoms of sodium and chorine. This would also be the case in rather extreme examples, e.g., the Na^{+11} and Cl^{+17} ions. Although this response is correct, it also seems a little unsatisfactory for the identity of chemical elements to depend on the nucleus of their atoms, given that all the chemical properties are supposed to be determined by the configurations and exchanges in the electrons around the nucleus.

23. This is perhaps why Mendeleev, a great defender of the nineteenth-century element scheme, was so reluctant to accept the notion of the transmutation of the elements discovered by Ernest Rutherford at the turn of the twentieth century.

24. The term refers to substance in the philosophical sense as discussed by Aristotle and then as recently as Spinoza and Kant, although each of these authors has rather different views on the question.

25. This is despite the fact that our present element scheme, which we owe to Paneth, was arrived at partly by his insistence on the distinction between abstract element and simple substance.

26. There is a certain irony here in that Mendeleev is really breaking away from Lavoisier in upholding the importance of the elements as basic substances, something that Lavoisier considered a sterile concept.

27. For a discussion of this point, see F.A. Paneth, The Epistemological Status of the Chemical Concept of Element, *British Journal for the Philosophy of Science*, 13, 1–14, 144–160, 1962. Also, the mere fact that Mendeleev and, considerably later, Paneth continue to maintain a dual nature for the elements attests to the fact that the chemical revolution did not eliminate the metaphysical view of elements.

28. My comments apply specifically to the first English translation of Mendeleev's book, or the fifth Russian edition.

29. The French translation lends itself more readily to making the distinction between element and simple substance, whereas in the English translation the word "element" is frequently used to mean simple body. It is not surprising, therefore, that the only extensive philosophical analysis of this distinction has been made by the French philosopher-historian Bernadette Bensaude-Vincent. The only other such analysis in modern times has been by Paneth, who used the German translation of Mendeleev's book, which likewise preserves the spirit of the distinction by speaking of simple body rather than using the word "element" indiscriminately.

30. D.I. Mendeleev, *The Principles of Chemistry*, 5th Russian ed., vol. 1, 1889 (1st English trans. by G. Kemensky, Collier, New York, 1891), p. 23.

31. The phrase "elements as principles" is also frequently used in the literature on the nature of elements.

32. This question has taken on a rather mundane sense in today's chemistry, namely, that every element, by which one actually means simple body, is characterized by a particular atomic weight or atomic number.

33. The dates of the eight Russian editions published during Mendeleev's lifetime are as follows: 1st ed., 1868–1871; 2nd ed., 1872–1873; 3rd ed., 1877; 4th ed., 1881–1882; 5th ed., 1889; 6th ed., 1895; 7th ed., 1903; 8th ed., 1906. A further five posthumous editions have been published in Russian, with some additions to cover more recent discoveries. The translations of Mendeleev's book are as follows: 1st English trans., 1891 (of the 5th Russian ed.); 2nd English trans., 1897 (of the 6th Russian ed.); 3rd English trans., 1905 (of the 7th

Russian ed.). In addition, the fifth Russian edition was translated into German in 1890 and the sixth Russian edition into French in 1895.

34. M. Kaji, Mendeleev's Conception of the Chemical Elements and the Principles of Chemistry, *Bulletin for the History of Chemistry*, 27, 4–16, 2002; M. Kaji, Mendeleev's Discovery of the Periodic Law: The Origin and the Reception, *Foundations of Chemistry*, 5, 189–214, 2003. Of course, many Russian scholars conducted such surveys before Kaji, but I am not aware of any that have been translated into English.

35. It is interesting to note that this is the first time in his book that Mendeleev actually treats a group of elements together in the same chapter, namely, chapter 11.

36. Even on this point, there were precursors, as mentioned in chapter 2. The first person to consider what might be termed horizontal relationships was Kremers.

37. Mendeleev, 1869, quoted in translation in H.M. Leicester and H.S. Klickstein, Dmitrii Ivanovich Mendeleev, *A Sourcebook in Chemistry, 1400–1900*, Harvard University Press, Cambridge, MA, 1952, pp. 439–444, quoted from p. 442.

38. Kaji cites Henry Leicester, William Brock, and Bernadette Bensaude-Vincent.

39. E.R. Scerri, J.W. Worrall, Prediction and the Periodic Table, *Studies in History and Philosophy of Science*, 32, 407–452, 2001.

40. I do not mean to imply that the weights of individual atoms can be directly observed. I intend this remark in the chemist's sense that stoichiometric reactions can be rationalized by appeal to atomic weights of participating elements.

41. As a matter of fact, the grouping together of the halogens had already been anticipated on chemical grounds in spite of their obvious visual differences. I merely cite this as an example of the unreliability, in general, of classification based on simple substances. J.H. Kultgen, one of very few philosophers to try to analyze Mendeleev's underlying assumptions, has supported the general philosophical approach I am emphasizing, in some respects. J.H. Kultgen, Philosophical Conceptions in Mendeleev's Principles of Chemistry, *Philosophy of Science*, 25, 177–183, 1958.

42. Many other chemists had already realized that chlorine, bromine, and iodine belong together in one group.

43. Gordin, *A Well-Ordered Thing,* Basic Books, New York, 2004*,* p. 228.

44. D.I. Mendeleev, The Periodic Law of the Chemical Elements, *Journal of the Chemical Society*, 55, 634–658, 1889, quoted from p. 644.

45. D.I. Mendeleev, *The Principles of Chemistry*, 3rd English translation, of 7th Russian edition, 1905, vol. 1, Longmans, London, p. 20.

46. F.A. Paneth, Chemical Elements and Primordial Matter, in H. Dingle, G.R. Martin (eds.), *Chemistry and Beyond*, Wiley, New York, 1965, pp. 53–72, quoted from pp. 56–57.

47. Of course, modern chemists are constantly referring to protons, neutrons, and electrons. I am making a more general point here that pertains more to the discovery of subnuclear structure, which can generally be ignored by the chemist.

48. G. Bachelard, *Le Pluralisme Cohérent de la Chimie Modèrne*, Vrin, Paris, 1932 (translation of quotation provided by the present author).

49. For further discussion of these issues, see E.R. Scerri, Realism, Reduction and the Intermediate Position, in N. Bhushan, S. Rosenfeld, *Of Minds and Molecules*, Oxford University Press, New York, 2000, pp. 51–72.

50. E.R. Scerri, Response to Vollmer's Review of Minds and Molecules, *Philosophy of Science*, 70, 391–398, 2003.

CHAPTER

5

PREDICTION AND ACCOMMODATION

The Acceptance of Mendeleev's Periodic System

Although periodic systems were produced independently by six codiscoverers in the space of a decade, Dmitri Mendeleev's system is the one that has had the greatest impact by far. Not only was Mendeleev's system more complete than the others, but he also worked much harder and longer for its acceptance. He also went much further than the other codiscoverers in publicly demonstrating the validity of his system by using it to predict the existence of a number of hitherto unknown elements.[1]

According to the popular story, it was Mendeleev's many successful predictions that were directly responsible for the widespread acceptance of the periodic system, while his competitors either failed to make predictions or did so in a rather feeble manner.[2] Several of his predictions were indeed widely celebrated, especially those of the elements germanium, gallium, and scandium, and many historians have argued that it was such spectacular feats that assured the acceptance of Mendeleev's periodic system by the scientific community.

The notion that scientific theories are accepted primarily if they make successful predictions seems to be rather well ingrained into scientific culture, and the history of the periodic table has been one of the episodes through which this notion has been propagated. However, philosophers and some scientists have long debated the extent to which predictions influence the acceptance of scientific theories, and it is by no means a foregone conclusion that successful predictions are more telling than other factors.

In looking closely at the bulk of Mendeleev's predictions in this chapter, it becomes clear that, at best, only half of them proved to be correct. This raises a number of questions. First of all, why is it that history has been so kind to Mendeleev as a maker of predictions? As historian of chemistry William Brock has pointed out, "Not all of Mendeleev's predictions had such a happy outcome; like astrologers' failures, they are commonly forgotten."[3] To put the question another way, why is it that Mendeleev's successful predictions served to bolster the validity of his system while his unsuccessful ones failed to undermine it?

If we accept that it was Mendeleev's predictions that carried the most weight in the acceptance of his periodic system, then we are at a loss to answer this question. But perhaps, as some have argued, it is by no means established that prediction is the single most important factor in demonstrating the validity of a new scientific idea.[4] In fact, rather than proving the value of prediction, the development and acceptance of the periodic table may provide us with a powerful illustration of the importance of accommodation, that is, the ability of a new scientific theory to explain already known facts.

From the time he first published his mature periodic system, in 1869, Mendeleev began to predict the existence of specific unknown elements and to correct the values of atomic weights of already known elements. Both of these forms of prediction were essential to the refinement of his system and are examined in the course of this chapter. Although the prediction of new elements and the correction of atomic weights of existing elements both represent forms of predictions, they are of a somewhat different character, an aspect that will be explored. The historian Stephen Brush has coined the apt phrase "contrapredictions" to describe the correction of already known elements.[5] He, too, believes that they represent a different category from the prediction of previously unknown elements.

The questions examined in this chapter are (1) whether the prediction of new elements by itself was as decisive a factor in the acceptance of Mendeleev's system as the popular accounts would have it, and (2) whether successful predictions in general (new elements and contrapredictions) had significantly more impact than did successful accommodations (the fitting of elements into the periodic system).[6]

Mendeleev's extraordinary proficiency as a chemist, combined with his unwavering belief in atomic weight as the supreme ordering principle among the elements, guided him in developing his system. His genius lay in his ability to sift intuitively through the mass of correct and incorrect knowledge of the elements that had accumulated to produce a system, an *idea*, that was both elegant and durable enough to withstand the chemical and physical discoveries that would follow its introduction.

Mendeleev's Approach

Mendeleev can be distinguished from his competitors by a lifelong devotion to, and love for, the individuality of the elements that went hand in hand with an intimate knowledge of their chemical characteristics. Whereas Julius Lothar Meyer, for example, seemed more concerned with physical properties in his own quest to arrive at a periodic classification, Mendeleev's approach can be described as a "natural history" of the elements.[7] Mendeleev's depth of knowledge of the elements was something most of today's chemists could not match.[8]

Contrary to many myths and legends, which would have us believe that Mendeleev arrived at the periodic system by juggling with playing cards and by tinkering with values of atomic weights, this was only a small part of the story.[9] The real work consisted in being very familiar with the chemical and physical properties of the building blocks from which the periodic system was to be fashioned. Mendeleev was expert in such matters and knew what kinds of salts all the elements were capable of forming and which reagents could be used to obtain precipitates from their salts. These and countless other details were synthesized and carefully weighed as evidence when he was deciding where to place any particular element.

It is important to understand Mendeleev's modus operandi regarding the placement of elements in the periodic system if we are to appreciate the motivation for many of his corrections of atomic weights and his predictions of unknown elements. Mendeleev considered a number of criteria in addition to atomic weight ordering, such as family resemblance among elements and the concept of the single occupancy of elements in any space in the periodic table. However, all these criteria could be, and often were, overridden as individual cases presented themselves to him.

Family resemblance among the elements was very important to Mendeleev. He looked for chemical similarities as revealed by reactions with other elements, the nature of salts, precipitation reactions, and the acid–base chemistry of the elements. In contrast to Lothar Meyer's approach, Mendeleev believed chemical properties should take precedence over physical criteria, with the important exception of atomic weight, of course. Lothar Meyer had established his own periodic system by concentrating predominantly on physical resemblance in properties, such as atomic volumes, densities, and fusibilities.[10] For Mendeleev, it was so important that chemically similar elements be grouped together that he was willing to violate the concept of single occupancy, according to which each place in the periodic table may contain only a single element. This was the case in what he labeled group VIII[11] of his table, where sets of three elements, for example, iron, cobalt, and nickel, occupied what should have been several single spaces.[12]

The strictest criterion Mendeleev employed was that of ordering elements according to increasing atomic weight. As noted in chapter 4, he had stronger philosophical reasons than the other discoverers of the periodic system for insisting on the fundamental role of atomic weight, so much so that he was willing to try to bend nature to fit his grand philosophical scheme. He would occasionally seem to violate even this principle, however, in cases where the chemical character of an element seemed to demand it. An example is his placement of tellurium before iodine, as the atomic weight of tellurium has the higher value of the two elements. But while making this reversal, Mendeleev did not just disregard the issue of atomic weight, but rather insisted that the atomic weight of at least one of these elements had to have been determined incorrectly and that future experiments would eventually reveal an atomic weight ordering in conformity with his placement of tellurium before iodine. Thus, Mendeleev's main guiding principle was that any apparent misplacement of an element in his original system, or those of others, was primarily the result of an incorrect atomic weight having been assigned to that element.

In some cases, Mendeleev would correct the atomic weights of a misplaced element, but there were also cases where he considered it sufficient to move an element in order to reflect more faithfully certain family resemblances, without changing the atomic weight in question. This is what Mendeleev did with mercury, which he came to regard as an analogue of zinc and cadmium rather than of copper and silver, as he had done in his earliest tables.[13]

There are many elements over which Mendeleev deliberated for considerable periods of time and published several accounts. These include indium, erbium, and lanthanum, all of which involved subtle arguments having to do with atomic weight corrections, some of which are examined next.

Correcting Atomic Weights

Correcting the atomic weight of an element sometimes involved changing the multiple employed for obtaining its atomic weight from its equivalent weight. The repositioning of elements by this method of atomic weight change would prove to be particularly successful for Mendeleev. In adopting an alternative multiple of the equivalent weight, what Mendeleev was doing was adopting an alternative valence for certain elements, in view of the relationship

$$\text{atomic weight} = \text{valence} \times \text{equivalent weight}$$

In some cases, the valence of an element could be determined only indirectly through group resemblance. Mendeleev used this approach in the cases of beryllium, uranium, indium, and thorium, among others. Any suggested changes in group resemblance had to be carefully considered in order to determine whether the resulting change in valence, and hence atomic weight, was really warranted. For example, in the case of uranium, the element did not form any compounds with hydrogen, thus removing any possibility of arriving at its valence in the most direct manner.[14] With other elements, uranium shows valences of 2, 3, 4, 5, 6, and even 8, variable valence being a common characteristic of transition metals. Mendeleev had to rely on uranium's other forms of chemical behavior to determine its group and to give it a primary valence of 4.

In other cases, Mendeleev called for a small adjustment in the equivalent weight, which in turn led to corresponding small changes in the value of the atomic weight on multiplication by the appropriate valence. Examples of this kind included titanium, tellurium, iodine, platinum, gold, cobalt, nickel, and potassium. The case of titanium is rather interesting because the element already had a secure place in the periodic table according to atomic weight ordering, as well as in terms of family resemblances with other elements. Nevertheless, Mendeleev chose to alter its atomic weight from 50 to 48 in order to create greater regularity among differences between the values of consecutive elements ordered by atomic weight.

Whether such regularity can be regarded as another of Mendeleev's criteria is open to question, given that he appears to have used it only in this single case. But the fact remains that Mendeleev was correct since the modern value for titanium is indeed closer to 48 than it is to 50. Mendeleev's uncanny sense for correcting atomic weights, which often seemed to defy logical reconstruction, served him well in this and other cases.[15]

Beryllium

The placement of the metal beryllium provided one of the most severe tests for Mendeleev's system. Its case proved to be historically significant because it involved a controversy that lasted a considerable period of time, ending with the complete vindication of Mendeleev's position. The question was whether the element should be assigned a valence of 2 or 3, which would affect its atomic weight and thus would in turn govern the position it took in the periodic table.

Stanislao Cannizzaro's method for determining atomic weights was not easy to apply to the metallic elements, as it required volatile compounds. Instead, other methods continued to be used for metals. One important way of obtaining atomic weights was through the 1819 law of Pierre-Louis Dulong and Alexis-Thérèse Petit. As discussed in chapter 2, these authors had found an approximate relationship between the specific heat and atomic weight of a solid element to be[16]

$$\text{atomic weight} \times \text{specific heat} = \text{a constant} = 5.96$$

The measured specific heat of 0.4079 for beryllium indicated an atomic weight of 14.6, which would place the element in the same group as the trivalent aluminum.[17]

In addition to atomic weight, there were other reasons to place beryllium with aluminum. Clues to beryllium's valence could be obtained by combining it with oxygen to create an oxide. Metal oxides or hydroxides dissolve in water to form bases, while nonmetal oxides or hydroxides dissolve in water to form acids. Moreover, the chemical characteristics of the oxides generally provide an approximate indication of the valence of the metal concerned according to certain rules. These are summarized below for any metal in general, denoted as M:

Low-valence oxides	MO, MO_2	Strongly basic
Intermediate-valence oxides	M_2O_3	Weakly basic
High-valence oxides	M_2O_5, MO_3	Acidic

Beryllium oxide is weakly basic, with a metallic structure unlike that of magnesium, and beryllium chloride is volatile just like aluminum chloride. Taking these facts together, the association of beryllium with aluminum appears to be compelling.

In spite of all this evidence, Mendeleev supported the view that beryllium is divalent using arguments that were purely chemical, as well as arguments based on the periodic system. He pointed out that beryllium sulfate presents a greater similarity to magnesium sulfate than to aluminum sulfate and that, whereas the elements analogous to aluminum form alums, beryllium fails to do so. He also argued that if the atomic weight of beryllium were about 14, it would not find a place in the periodic system. Mendeleev noted that such an atomic weight would place beryllium near nitrogen, toward the right side of the table, where it should show distinctly acidic properties and have higher oxides of the type Be_2O_5 and BeO_3, which is not the case. Instead, Mendeleev argued that the atomic weight of beryllium might be approximately 9, which would place it between lithium (7) and boron (11) in the periodic table, and thus put it in group II.

In 1885, the issue was finally settled conclusively in favor of Mendeleev by measurements of the specific heat of beryllium at elevated temperatures. The specific heat of any element increases with temperature, and as a result, the constant value that appears in Dulong and Petit's law is achieved only if the measurements are carried out at high temperatures. This finding became appreciated soon after the discovery of Dulong and Petit's law and allowed more accurate measurements of atomic weight to be made. Further experiments with beryllium pointed to an atomic weight of 9.0, in reasonable agreement with Dulong and Petit's law, and supported the divalence of the element as Mendeleev had argued.[18]

Uranium

One of Mendeleev's boldest atomic weight changes was in the case of uranium, where the atomic weight was changed by a whole multiple. The element uranium was first isolated in 1841 by Eugène Peligot in France. In his famous first table of 1869, Mendeleev placed the element, with its assumed weight of 116, between cadmium at 112 and tin at 118, thus making it a chemical analogue of boron and aluminum in group III of the table.

Mendeleev avoided using Cannizzaro's atomic weight of 120 for uranium, for such a value would not have allowed him to place it in the periodic table. If uranium had an atomic weight of 120, it would need to be placed between tin (118) and antimony (122). These two elements show valences of 4 and 3, respectively, and so the inclusion of uranium between them would have violated the gradual decrease in valence on moving across the elements in group IV through group VII.[19] In addition, the placement of both tin and antimony appeared quite secure and in little doubt. Tin was in the same group as silicon and lead, both of which show valences of 4, and antimony was in the same group as phosphorus, arsenic, and bismuth, all of which show valences of 3.

In an early manuscript table, Mendeleev designated uranium as "U 120" and listed it outside the table at the foot of the page. Later he crossed this out and replaced it with "U 116?" placed in the main body of the table between cadmium and tin. This place should have been filled by the element indium, but Mendeleev also initially misplaced this element because he wrongly assumed that its atomic weight was 75.6.

In the spring of 1869, Mendeleev personally undertook the experimental study of the atomic volume of uranium with the object of resolving the uranium problem. He decided that the element did not in fact fit between cadmium and tin, and he considered that Cannizzaro's value of 120 might indeed be correct. Now he was back where he had started, with no place for uranium in the table, so he suggested again that perhaps there had been an error in the determination of its atomic weight. This time he proposed that the value should be doubled because the high density of uranium (18.4) was typical of heavy-atomic-weight elements such as platinum (197), osmium (199), and iridium (198). He then set his assistant Bohuslav Brauner the task of measuring the specific heat of uranium, but since the results were somewhat inconclusive, Mendeleev announced the atomic weight modification without the support of experimental evidence.

In conceptual terms, the doubling of Cannizzaro's value was not as great a leap as it might appear. Since atomic weight is a product of valence and equivalent weight, all that was required in doubling uranium's atomic weight was for its valence to be regarded as double what it was previously thought to be, namely, 6 instead of 3. Mendeleev argued that uranium, which forms UO_3, is analogous to chromium, which forms CrO_3. He therefore began grouping uranium with chromium.

In late 1870, Mendeleev actually placed "U = 240" for the first time in the periodic table. Experimental support for the corrected atomic weight of uranium came later, in 1874, from Henry Roscoe in England. It took its place as a higher chemical analogue of chromium, molybdenum, and tungsten, where it remained throughout the rest of Mendeleev's life and indeed until the middle of the twentieth century. Eventually, American chemist Glenn Seaborg's discovery of the actinide series prompted a major readjustment of the periodic table, which included the repositioning of uranium.[20]

Tellurium and Iodine

The case of tellurium and iodine is one of only four pair reversals in the periodic system and the best known among them. Many historical accounts make a point of recounting how astute Mendeleev was to reverse the positions of these elements, thus putting chemical properties over and above the ordering according to atomic weight. In doing so, these accounts err in several respects. First of all, Mendeleev was by no means the first chemist to make this particular reversal. As mentioned in chapter 3, William Odling, John Newlands, and Julius Lothar Meyer all published tables in which the positions of tellurium and iodine had been reversed, well before the appearance of Mendeleev's articles. Second, Mendeleev was not, in fact, placing greater emphasis on chemical properties than on atomic weight ordering in this case. Mendeleev held to his criterion of ordering according to increasing atomic weight and repeatedly stated that this principle would tolerate no exceptions. Mendeleev's thinking regarding tellurium and iodine was rather that the atomic weights for one or both of these elements had been incorrectly determined and that future work would reveal that even on the basis of atomic weight ordering tellurium should be placed before iodine. On this point, as in many instances that tend to go unreported, Mendeleev was wrong.

But let us look into the historical sequence of events regarding tellurium and iodine, since it is only by examining the circumstances closely that the reader can obtain a clear notion of the nature of the work in which Mendeleev and other pioneers of the periodic system were engaged. At the time when Mendeleev proposed his first periodic system, the atomic weights for tellurium and iodine were thought to be 128 and 127, respectively. Mendeleev's belief that atomic weight was the fundamental ordering principle meant that he had no choice but to question the accuracy of these two values. This was because it was clear that, in terms of chemical similarities, tellurium should be grouped with the elements in group VI and iodine with those in group VII or, in other words, that this pair of elements should be "reversed." Mendeleev continued to question the reliability of these atomic weights until the end of his life. This was one problem he was not able to solve.

Initially, Mendeleev doubted the atomic weight of tellurium while believing that the atomic weight of iodine was essentially correct. He began to list tellurium as having an atomic weight of 125 in some of his subsequent periodic tables. At one time, he asserted that the commonly reported value of 128 was the result of measurements having been made on a mixture of tellurium and a new element he called eka-tellurium. Prompted by these pronouncements, Bohuslav Brauner began a series of experiments in the early 1880s aimed at the redetermination of the atomic weight of tellurium. By 1883, he was able to report that the value for tellurium should be 125. Mendeleev was duly sent a telegram of congratulations by other participants present at the meeting at which Brauner had made this announcement. In response, Mendeleev went as far as to list Brauner as one of the four "consolidators" of the periodic law in 1886. In 1889, Brauner obtained new results that seemed to further strengthen the earlier finding that the atomic weight of tellurium is 125.

But in 1895, everything changed as Brauner himself began reporting a new value for tellurium that was greater than that of iodine, thus returning matters to their initial starting point. Mendeleev's response was now to begin to question the accuracy of the accepted atomic weight value for iodine instead of tellurium. This time he requested a redetermination for the atomic weight of iodine and hoped that its value would turn out to be higher. In some of his later periodic tables, Mendeleev listed tellurium and iodine as both having atomic weights of 127. Clearly, the real story is far more complicated than is usually reported, and in the final analysis, it does not appear to further Mendeleev's reputation very much, since the atomic weight of tellurium simply *is* higher than that of iodine. The problem would not be resolved until 1913 and 1914 by Henry Moseley, who showed that the elements should be ordered according to atomic number rather than atomic weight. While tellurium has a higher atomic weight than iodine, it has a lower atomic number, and this is why it should be placed before iodine in agreement with its chemical behavior.

Mendeleev's Predictions

As is well known, Mendeleev successfully predicted the existence of several unknown elements. He arrived at his conclusions mainly through interpolation among atomic weights as well as among other chemical and physical properties. In a few cases he also used extrapolations, but only while warning of the less secure basis of this form of activity, since there is no guarantee that the trend shown among the measured data points will extend into regions where no measurements have been made.

In the case of interpolations, Mendeleev was attempting to fill in prescribed gaps in the table among elements that had already been placed and in many cases were well characterized. In his earliest periodic tables, those of 1869, these unknown elements were represented by dashes or a predicted atomic weight value accompanied by a question mark, for it was clear to Mendeleev that there must be elements that would fill these gaps. As described below in some detail, Mendeleev was able to predict many of the characteristics of these unknown elements very successfully. By contrast, extrapolating the existence of unknown elements was a much more tenuous process, and there was no assurance that this process was warranted. Mendeleev would later make use of such extrapolations and, not surprisingly, was rather unsuccessful in these cases.

Mendeleev first focused on two gaps in the periodic table, one below aluminum and one below silicon, and proposed to fill them with new elements. Such gaps were more or less demanded by the vertical grouping of the known elements that surrounded them. The known elements could not be moved around at will because they had to fit together according to chemical similarities. Gaps in the horizontal sequence of increasing atomic weights might also suggest the presence of a missing element, though not as reliably since the increase in atomic weights is not perfectly uniform even among a complete sequence of known elements.[21]

The first hint of these famous predictions was published along with his original table of 1869, when Mendeleev declared, "We must expect the discovery of yet unknown elements, e.g. elements analogous to Al and Si, with atomic weights 65–75."[22] In a talk to the Moscow Congress of the Russian Scientists and Physicians a couple of months later, Mendeleev stated that "those two elements which are still missing from the system and which show a resemblance to Al and Si, and have atomic weights of about 70, will have atomic volumes of 10 or 15, i.e. will have specific gravities of about 6,"[23] but he thought the lighter of these two might be indium, a known element.

In the autumn of 1870, Mendeleev had also begun to look for an element analogous to boron, and he listed the atomic volumes of these three elements to be[24]

eka-boron	eka-aluminum	eka-silicon
15	11.5	13

Subsequent manuscripts listed the atomic weights for these three elements as 44, 68, and 74, respectively, and a little later as 44, 68, and 72.

In early 1871, Mendeleev published a list of detailed predictions on each element for the first time. It was also in this paper that he now referred to them provisionally as eka-boron (scandium), eka-aluminum (gallium), and eka-silicon (germanium).[25] These were his most celebrated cases, and he was able to predict their chemical and physical properties to an astonishing degree. It would take 15 years from the time of these detailed predictions for all three of these new elements to be isolated and characterized, but in the end Mendeleev would be almost completely vindicated.

Mendeleev could interpolate many of the properties of his predicted elements by considering the properties of the elements on each side of the missing element and hypothesizing that the properties of the middle element would be intermediate between its two neighbors. Sometimes he took the average of all four flanking elements, one on each side and those above and below the predicted element. This interpolation in two directions was the method he used to calculate the atomic weights of the elements occupying gaps in his table, at least in principle.

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly illustrates his method using the known element selenium as an example. The atomic weight of selenium was known at the time and so could be used to test the reliability of his method. Given the position of selenium and the atomic weights of its four flanking elements:

	S (32)	
As (75)	Se ?	Br (80)
	Te (127.5)	

the flanking atomic weights can be averaged to yield approximately the correct value for the atomic weight of selenium:

$$\left(32 + 75 + 80 + 127.5\right) / 4 = 79$$

However, Mendeleev did not always operate according to this clear procedure, even in the case of some of his most famous predictions. For example, if his method is applied to predicting the atomic weights, atomic volumes, densities, and other properties of gallium, germanium, and scandium, it produces values that differ significantly from those Mendeleev actually published. Employing Mendeleev's stated method of taking an average of the atomic weights of four flanking elements around gallium, using the atomic weights available at the time, gives a prediction of 70.9. In fact, Mendeleev modified this value to "about 69" by means of a more complicated averaging method that he explained only briefly in a single German publication.[26] The accepted value of the atomic weight of gallium at the time of its discovery was 69.35.

Table 5.1 contains Mendeleev's predicted properties of eka-aluminum, subsequently named gallium, as well as the observed properties of the element.[27]

TABLE 5.1
The predicted and observed properties of eka-aluminum (gallium).

Eka-aluminum	*Gallium*
General character: Properties should represent the mean of those of Zn and eka-silicon on the one hand, and those of Al and In on the other.	Many properties do indeed represent a transition from those of Zn to those of Ge on the one hand, and from those of Al to those of In on the other.
More acidic than eka–boron.	More acidic than scandium.
Atomic weight: ca. 68 (H = 1).	Measured atomic weight: 69.2 (H = 1).
Free element: A metal, which should be fairly easily obtained by reduction using C or Na. Its properties should in all respects represent a transition from those of metallic Al to those of metallic In. E.g., it will be more volatile than metallic Al, less so than metallic In.	Melting point 29.78 (lower than both In, 157°C, and Al, 660°C; I return to this point below). Boiling point is high, probably above 2,000°C; it probably falls between that of Al and In, but recorded figures are so discordant that this cannot be claimed with certainty.
Specific gravity: ca. 6.0 (atomic volume: ca. 11.5)	Specific gravity: 5.9 (atomic volume: 11.8)
Further predictions in 1875: Metal easily obtained by reduction. Will melt at quite a low temperature. Almost involatile. Not oxidized on contact with air. When heated to red-heat, should decompose water. The pure and fused metal will be only slowly subject to the action of acids and bases.	The metal is not oxidized in air at ordinary temperatures. Action on steam unknown. Gallium metal dissolves slowly in acids and alkalis.
Oxides and hydroxides: Formula of oxide, Ea_2O_3. The hydrous oxide will dissolve in KOH solution. Manuscript table of summer 1871 gives specific volume of oxide as "33?" Further Predictions in 1875: Specific Gravity of oxide, ca. 5.5. Basic properties more distinct than Al_2O_3, less than for ZnO; we should	The stable oxide is Ga_2O_3, gallic oxide. This is soluble in HCl, H_2SO_4, and aqueous alkali hydroxide and ammonia, but if it has been previously strongly heated, it dissolves in these media only extremely slowly. Barium carbonate precipitates the hydroxide from aqueous solutions of gallium salts. The hydroxide dissolves in aqueous acids and alkalis.

continued

TABLE 5.1
(*Continued*)

Eka-aluminum	*Gallium*
therefore expect it to be precipitated by $BaCO_3$ Soluble in strong acids. Should form an amorphous hydrate that is insoluble in water but that will dissolve in acids and alkalis.	
Halides: Should give a volatile anhydrous chloride, which is more soluble than aluminum salts. Eka-aluminum will certainly form alums. Its sulfide, Ea_2S_3, will be insoluble in water and will probably be precipitated by ammonium sulfide. It should give volatile organometallic compounds. 1875: Eka-aluminum will form neutral and basic salts $Ea_2(OH,X)_6$, but not acidic salts. The alum $EaK(SO_4)_2 \cdot 12H_2O$ will be more soluble than the corresponding aluminum salt and have less tendency to crystallize. The sulfide Ea_2S_3 or oxysulfide $Ea_2(S,O)_3$ should be precipitated by H_2S and will be insoluble in ammonium sulfide.	Anhydrous gallic chloride fumes in moist air; it is hydrolyzed by water with a hissing sound, though less violently than is aluminum chloride. Boiling point, 200°C. $ZnCl_2$ boils at 730°C. Gallic salts are even more strongly hydrolyzed in solution than are those of aluminum. Gallium forms alums. Ga_2S_3 is not precipitated by H_2S or $(NH_4)_2S$ in the absence of other metals in the solution.[2] It is, however, also quantitatively carried down with a number of other metallic sulfides (e.g., ZnS) when they are precipitated from alkaline or acetic acid solutions by H_2S. It is similarly precipitated with ZnS and other metallic sulfides by $(NH_4)_2S$. Gallium forms a basic sulfate in addition to the neutral sulfate. It does not form acid salts. Gallium gives volatile organometallic compounds.
Points relating to discovery:	
Eka-aluminum is likely to be discovered spectroscopically (on the grounds of its expected volatility), like In and Tl.	Gallium was indeed discovered spectroscopically.

Table reproduced from J.R. Smith, *Persistence and Periodicity*, unpublished Ph.D. thesis, University of London, 1975, 357–359.

The Discovery of Gallium

Eka-aluminum, or gallium as it was subsequently called, was discovered by French chemist Paul-Émile Lecoq De Boisbaudran in 1875. De Boisbaudran had been studying the spectra of the elements for a period of 15 years prior to making the discovery. He was aware of the fact that elements in the same family, or group, show the same general spectral features. De Boisbaudran did *not* discover gallium as a result of testing Mendeleev's prediction, however. Instead, he operated quite independently by empirical means, in ignorance of Mendeleev's prediction, and proceeded to characterize the new element spectroscopically. After working with 52 kg of zinc blende for a period of about 18 months, De Boisbaudran was able to observe a few spectral lines that had never been observed before, although he was unable to isolate the element. But following a further three months of work, using an additional several hundred kilograms of the same ore, De Boisbaudran isolated about a gram of the new element and reported his findings in the *Comptes Rendus de L'Académie des Sciences*.[28]

On reading a Russian translation of this paper, Mendeleev sent a note to the journal claiming that this was the element he had predicted and provisionally named eka-aluminum. De Boisbaudran at first reacted suspiciously to this claim, apparently believing that Mendeleev was asserting priority over the discovery of the element. He initially maintained that his own element had significantly different properties from those of the element predicted by Mendeleev, although he later changed his mind on this score.[29] De Boisbaudran did, however, continue to insist that his discovery of gallium involved empirical techniques quite separate from anything related to Mendeleev's work and that prior knowledge of it would, if anything, have hindered his discovery of the new element. He named the new element gallium after the Latin word for France.[30] As it turned out, the remaining two of Mendeleev's three famous predictions would also result in new elements named from other European countries, namely, eka-boron, which became scandium, and eka-silicon, which was named germanium.

In a note to the French journal,[31] Mendeleev repeated some of his earlier predictions and made several new ones. Interestingly, one of these newer predictions was rather dubious, and it is surprising that Mendeleev should have claimed it as a prediction. He claimed to predict that eka-aluminum oxide would be precipitated from aqueous solutions of eka-aluminum salts by barium carbonate. In fact, Mendeleev already knew that this was the case for the simple reason that it had already been reported by De Boisbaudran and, worse yet, Mendeleev himself had acknowledged this observation of the precipitation by $BaCO_3$ in a published note!

On a quite separate issue, Mendeleev had predicted in 1871 that eka-aluminum, or gallium, would "in all respects" have properties intermediate between those of the elements above and below it, namely, aluminum and indium. However, the melting point of gallium (30°C) is nowhere close to being intermediate between those of aluminum (660°C) and indium (155°C). In 1879, Mendeleev gave what appears to be an ad hoc rationalization of the anomalously low melting point for gallium. He first emphasized that gallium does indeed have an anomalously low melting point and that it can even melt in the hand. He then claimed that this was not unexpected since it could be rationalized by looking at trends within groups of elements on either side of the group containing gallium.

At this point, Mendeleev gave this fragment table:

Mg	Al	Si	P	S	Cl
Zn	Ga	...	As	Se	Br
Cd	In	Sn	Sb	Te	J

and claimed that for the group containing magnesium, zinc, and cadmium, the element with the lowest atomic weight, magnesium, had the highest melting point. On the other hand, Mendeleev stated that in the case of the group at the right-hand side of this fragment table, it was the element with the highest atomic weight, namely, iodine (J), that had the highest melting point.

Mendeleev then made an almost comical claim that elements falling in a group between these two groups should show intermediate behavior in that it should be the middle element of the group that shows the highest melting point. This supposedly explained why gallium, which lies in the middle column flanked by aluminum and indium, would be "expected" to show the lowest melting point of the three. In his words:

> In a transitory group such as Al, Ga, In, *we must* expect an intermediate phenomenon; the heaviest (In) and the lightest (Al), should be less fusible than the middle one, which is as it is in reality.[32]

Not only had such ad hoc arguments ever before been given by Mendeleev as a means of predicting trends in properties, but it also runs contrary to the spirit of his method of simple interpolation, which he used so successfully in many other instances. The ad hoc nature of the argument is compounded by the fact that it is by no means clear that the lesser fusibility of indium and aluminum truly represents "an intermediate phenomenon" with respect to the other groups mentioned. Nor is it clear why this somewhat contrived trend should begin at this particular place in the periodic table. In spite of his use of the word "must," there is nothing in the least bit compelling about Mendeleev's argument. Although nobody would consider denying Mendeleev his triumphs because of such indiscretions, we need to acknowledge that he also had some failings.

Scandium

Scandium was discovered in 1879 by the Swedish chemist Lars Fredrik Nilson, in a mineral ore called euxenite. It was identified as Mendeleev's predicted eka-boron by a French chemist, Pierre Clève. The discoverer, Nilson, promptly named the new element scandium after Scandinavia, where the ore had first been discovered.

Although it was not discovered spectroscopically, contrary to Mendeleev's prediction, the properties of the new element were very close to what Mendeleev had listed for eka-boron (table 5.2).

TABLE 5.2
The predicted and observed properties of eka-boron (scandium).

Properties predicted for eka-boron (Eb) by Mendeleev	*Properties found for Nilson's scandium (Sc)*
Atomic weight 44.	Atomic weight 44.
It will form an oxide Eb^2O^3 of specific gravity 3.5; more basic than alumina, less basic than yttria or magnesia; not soluble in alkalis; it is doubtful if it will decompose ammonium chloride.	Scandium oxide Sc_2O_3, has a specific gravity of 3.86; is more basic than alumina, less basic than yttria or magnesia. It is not soluble in alkalis; and does not decompose ammonium chloride.
The salts will be colorless and give gelatinous precipitates with potassium hydroxide and sodium carbonate. The salts will not crystallize well.	Scandium salts are colorless and give gelatinous precipitates with potassium hydroxide and sodium carbonate. The sulfate does not crystallize well.
The carbonate will be insoluble in water and probably be precipitated as a basic salt.	Scandium carbonate is insoluble in water.
The double alkali sulfates will probably not be alums.	The double alkali sulfates are not alums.
The anhydrous chloride, $EbCl_3$, should be less volatile than aluminum chloride, and its aqueous solution should hydrolyze more readily than that of magnesium chloride.	Scandium chloride, $ScCl_3$, begins to sublime at 850°C. Aluminum chloride begins to sublime at more than 100°C. In aqueous solution the salt is hydrolyzed.
Eka-boron will probably be discovered spectroscopically.	Scandium was not discovered spectroscopically.

Table adapted from P. Clève, Sur le Scandium, *Comptes Rendus des Seances de l'Académie des Sciences*, 89, 419–422, 1879, tables from pp. 421–422.

Germanium

Another of Mendeleev's most successful predictions, eka-silicon, was discovered by Clemens Winkler in 1886 and named germanium. Winkler and other confirmers of the periodic law, as Mendeleev called them, are shown in figure 5.1. The manner in which germanium was connected with Mendeleev's prediction of eka-silicon is rather interesting because it shows the complications that were involved in such cases.

Germanium was not immediately identified with Mendeleev's eka-silicon. Winkler initially believed that he had discovered another of Mendeleev's predictions, eka-stibium, an element that was supposed to be placed between stibium (antimony) and bismuth. Mendeleev responded to this claim by publishing a paper[33] in which he gave a revised account of the properties expected of eka-stibium in order to argue that Winkler had not in fact found this element. Mendeleev believed that the new element was to be identified with yet another of his predictions, eka-cadmium, which he believed would lie between cadmium and mercury. Victor von Richter, from Breslau, Germany, then wrote to Winkler to suggest that the new element might in fact be Mendeleev's eka-silicon. At about the same time, Lothar Meyer agreed with von Richter and further pointed out that this element coincided with his own predictions for a new element. So it was that Winkler went back to work on isolating larger quantities of the element and, on further characterization, was able to announce that it was indeed Mendeleev's predicted eka-silicon. Table 5.3 summarizes the main predictions as well as the findings on this element.

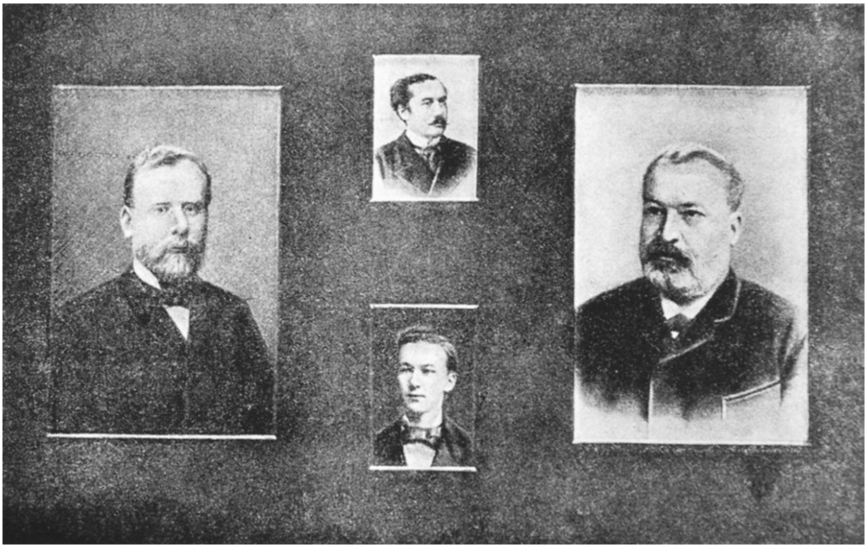


FIGURE 5.1 The confirmers of the periodic law. Clockwise from left: Nilson, De Boisbaudran, Winkler, and Brauner. Photo and permission provided by Gordon Woods.

TABLE 5.3

The predicted and observed properties of eka-silicon (germanium).

Property	*Eka-silicon 1871 prediction*	*Germanium discovered 1886*
Relative atomic mass	72	72.32
Specific gravity	5.5	5.47
Specific heat	0.073	0.076
Atomic volume	13 cm^3	13.22 cm^3
Color	Dark gray	Grayish white
Specific gravity of dioxide	4.7	4.703
Boiling point of tetrachloride	100°C	86°C
Specific gravity of tetrachloride	1.9	1.887
Boiling point of tetraethyl derivative	160°C	160°C

Although Mendeleev had foreseen a number of properties, as table 5.3 shows, he had been wrong in thinking that the element would be difficult to liquify and difficult to volatilize, whereas Lothar Meyer's predictions on these points had been correct. Clearly, Mendeleev was spectacularly successful in these predictions, but perhaps not quite to the extent that is implied by the more selective tables of comparison that regularly appear in chemistry textbooks and even histories of chemistry.

Mendeleev's Less Successful Predictions

In his later years, Mendeleev devoted considerable attention to elements occurring before hydrogen in the periodic table. He gave a number of reasons for taking such a possibility seriously: First of all, the discovery of a whole new series of elements, the noble gases, in the closing years of the nineteenth century led him to think that this series could be extended upward to earlier analogues of the first two noble gases, helium and neon. Second, the apparent success of the ether theory in optical physics suggested to him that ether should be identified as a new element, which he chose to call newtonium.[34] Third, ether would have to lack the ability for chemical combination since it was believed to permeate all substances. In addition, the notion of a completely unreactive element had become highly plausible after the discovery of the unreactive noble gases.

Mendeleev predicted the existence of two elements lighter than hydrogen, calling them elements x and y, based on numerical relations between atomic weight ratios in a periodic table, which he devised in 1904 (table 5.4).

In order to predict the atomic weight of the ether (newtonium), or element x, Mendeleev considered the atomic weight ratios of the known noble gas elements:

Table 5.4
Fragment of Mendeleev's periodic table of 1904 showing the positions of predicted elements x and y.

x	
y	H = 1.008
He = 4.0	Li = 7.03
Ne = 19.9	Na = 23.05
Ar = 38	K = 39.1
	Cu = 63.3
Kr = 81.8	Rb = 85.4

D.I. Mendeleev, *An Attempt Towards a Chemical Conception of the Ether*, Longmans, Green & Co., London, 1904, table on p. 26.

$$\mathrm{Xe : Kr = 1.56,\ Kr : Ar = 2.15,\ Ar : He = 9.5}$$

From these figures, he extrapolated the ratio He:Newt = 23.6, thus giving an atomic mass of 0.17 for newtonium.[35]

To estimate the atomic weight for the element that he designated as y, Mendeleev considered the ratios of atomic weights for the first two members of adjacent groups in the periodic table. He noted that the value for this ratio decreased smoothly from left to right:

Ne:He	Na:Li	Mg:Be	Al:B	Si:C	P:N	S:O	Cl:F
4.98	3.28	2.67	2.45	2.37	2.21	2.00	1.86

Extrapolating from the atomic weight of newtonium and the additional ratio of Li:H = 6.97, Mendeleev estimated that the ratio of He:y should be at least 10, from which he deduced a value of at least 0.4 for element y. Thus, it would seem that Mendeleev, who had earlier avoided any involvement with numerical relationships concerning triads, had now also succumbed to a very similar form of numerology.[36] Indeed, he asserted this claim in the strongest possible terms:

> At the present time, when there remains not the slightest doubt that group I, which contains hydrogen, is preceded by a zero group containing elements of lesser atomic weights than the elements of group I, it seems to me *impossible* to deny the existence of elements lighter than hydrogen.[37]

But Mendeleev's elements x and y would never be found.

The discovery of the noble gases at the turn of the twentieth century also suggested to Mendeleev the possible presence of six new elements between hydrogen and lithium, as he indicated in his periodic table of 1904. In one of these cases, Mendeleev was more specific; namely, he predicted a possible analogue of the halogen fluorine. He claimed that the new element would serve to restore symmetry to the table by making the number of halogens five, to coincide with the five known alkali metals. Once again, we are forced to conclude that Mendeleev was mistaken about these predictions, since none of the six elements were subsequently discovered.

Mendeleev made a number of other unsuccessful predictions. In two unpublished tables dated 1869, he made two entries indicating elements he thought would be discovered: ? = 8 and ? = 22. As with some of his other predictions of atomic weights of new elements, Mendeleev gave no indication of how he arrived at these predicted values, which were later removed and never appeared again in published form. Mendeleev also predicted the occurrence of elements with atomic weights of 2, 20, and 36, which, again, were never found.

In addition, he predicted lighter analogues of calcium and explicitly ruled out beryllium and magnesium as occupying these places.[38] This proved to be another mistake in that both beryllium and magnesium are indeed the missing analogues of calcium, which Mendeleev had misplaced elsewhere in his original tables.

One cannot help speculating as to the cause of these unfortunate cases. It appears that Mendeleev was relying exclusively on atomic weight calculations and was disregarding the many subtle chemical clues that had guided him so well in his successful cases. As Jan van Spronsen has aptly commented, Mendeleev's approach in these unsuccessful cases "stands as a warning to the investigators when applying the deductive scientific method exclusively."[39]

Unlike in physics, chemical reasoning does not generally proceed unambiguously from general principles. Chemistry is a more inductive science in which large amounts of observational data must be carefully weighed before reaching any conclusion, as Mendeleev had previously done when correcting atomic weights and predicting new properties by interpolation among known elements. The cases under consideration here seem to represent the speculations of an elderly and established scientist with nothing to lose. Here Mendeleev is not being guided by the chemical intuition that had served him so well in the past but is venturing into the less familiar field of attempting to produce new elements by deduction.

It is puzzling that Mendeleev's unsuccessful predictions do not seem to have counted against the acceptance of the periodic system.[40] There seem to have been as many as 10 failed predictions of elements by Mendeleev. In fact, if one considers all of Mendeleev's predictions, it appears that he was successful in only half of them. This fact has not been given much consideration, as it is much more common for scholars to be impressed by his dramatic successes.

Table 5.5 lists all of Mendeleev's firm predictions. It contains only the elements to which he gave provisional names.[41] Thus, it does not include elements such as astatine and actinium, which he predicted successfully but did not name. Neither does it include predictions that were represented just by dashes in Mendeleev's periodic systems. Among some other failures, not included in the table, is an inert

TABLE 5.5
List of Mendeleev's major predictions, successful and otherwise.

Element as given by Mendeleev	*Predicted atomic weight*	*Measured atomic weight*	*Eventual name*
Coronium	0.4	Not found	Not found
Ether	0.17	Not found	Not found
Eka–boron	44	44.6	Scandium
Eka–cerium	54	Not found	Not found
Eka–aluminum	68	69.2	Gallium
Eka–silicon	72	72.0	Germanium
Eka–manganese	100	99	Technetium (1939)
Eka–molybdenum	140	Not found	Not found
Eka–niobium	146	Not found	Not found
Eka–cadmium	155	Not found	Not found
Eka–iodine	170	Not found	Not found
Eka–caesium	175	Not found	Not found
Tri–manganese	190	186	Rhenium (1925)
Dvi–tellurium	212	210	Polonium (1898)
Dvi–caesium	220	223	Francium (1939)
Eka–tantalum	235	231	Protactinium (1917)

Compiled by the author.

gas element between barium and tantalum, which would have been called eka-xenon, although Mendeleev did not refer to it as such.

A success rate of half is clearly not outstanding by any stretch of the imagination.[42] The fact that Mendeleev made as many failed predictions as successful ones seems to belie the notion that what counted most in the acceptance of the periodic system were Mendeleev's successful predictions.

The Acceptance of Mendeleev's Periodic System

As mentioned in chapter 4, Mendeleev's mature periodic system first appeared in print in 1869 in the Russian chemical literature, and a German abstract of the article appeared in the same year. This was followed by a number of German translations of his articles in 1871. The first English announcement of an article by Mendeleev appeared in 1871 in the journal *Chemical News*.[43] French translations began appearing in 1875. Although his textbook *The Principles of Chemistry* did not appear in German until 1890, in English until 1891, or French until 1895, most European chemists would have heard of the new system much sooner through Mendeleev's various journal articles.

Many historians have argued that despite its prompt publication in the major European languages, Mendeleev's system did not attract much attention until the discovery of gallium by De Boisbaudran in 1875. Some point to this delay to suggest that it was Mendeleev's successful predictions that paved the way for the acceptance of his periodic system.[44] While there is no doubt that his predictions of gallium, germanium, and scandium, especially, received much attention, the question is whether these predictions and others greatly outweighed the system's many successful accommodations in bringing about its acceptance. In fact, a careful examination of the events following the system's first appearance in 1869 reveals that they may not have done so.

Mendeleev was awarded the prestigious Davy Medal in 1882, after gallium and scandium had been discovered. The philosophers Patrick Maher and Peter Lipton have pointed to this award as proof that it was not until Mendeleev's predicted elements had begun to be discovered that his system received the recognition it deserved. They take this to indicate that prediction weighed much more heavily than accommodation in the acceptance of the periodic system. In fact, Lipton goes so far as to say, "Sixty accommodations [the placement of the known elements] paled next to two predictions."[45]

Maher and Lipton both imply that there was a time lag between Mendeleev's accommodation of the known elements, in his construction of the periodic system, and his prediction of the three unknown elements. The existence of such a time lag is important to their argument. If it had not occurred, and the accommodations and predictions had been made in the same paper, it would be very difficult to ascertain whether the acceptance of Mendeleev's scheme rested primarily on its ability to accommodate or to predict.

In fact, Lipton, in paraphrasing Maher, claims quite specifically that when Mendeleev accommodated the 60 known elements (it should be 62), "the scientific community was only modestly impressed,"[46] thus clearly indicating a supposed time lag between the initial accommodation and later predictions. Maher implies such a time lag between accommodation and prediction by dating the predictions to 1871. Both of these authors are committing a historical fallacy relevant to the central issue, however, for although he did not give them names until 1871, Mendeleev left gaps for eka-boron, eka-aluminum, and eka-silicon, with their predicted atomic weights, when he first announced his periodic system in his famous paper of 1869. And in 1869 and 1870, he predicted their atomic volumes and specific gravities. Thus, the time lag that Maher and Lipton imply did not in fact take place.

The only justification Maher and Lipton might have for concentrating on the 1871 article is that it contained Mendeleev's first set of detailed predictions. Another factor may be that it was not until this paper that Mendeleev gave his predicted elements provisional names. But it is hard to imagine that Maher and Lipton would claim the 1871 predictions as more definitive than those of 1869 from the mere fact that Mendeleev was only then prepared to give the elements names, and provisional ones, at that. The whole question of prediction is fraught with problems. For example, should we consider predictions made in unpublished manuscripts or a talk given to a learned society? Similarly, one might well ask just how detailed the prediction itself should be to count as a true prediction.

In any case, Maher and Lipton were not the first to suggest there was such a time lag between Mendeleev's original announcement of the periodic system and his predictions of unknown elements. Other historians, too, have conveyed the impression that Mendeleev's predictions were decisive in the acceptance of the periodic table, but they regularly fail to cite reactions by chemists at the time that might support this view.[47] This is, of course, the crucial issue, namely, whether the scientific community values predictions above explanations of already known facts, and not what later historians might report. It would seem that these historians are merely reconstructing the course of events while incorporating the popular myth regarding predictions, and that Maher and Lipton have recently revived this view in the philosophical literature. Of course, the fact that Mendeleev's accommodations and predictions were published simultaneously does not rule out the Maher–Lipton position that scientists attach more importance to predictions. But to maintain their claim, these authors would need to cite historical evidence to the effect that scientists did indeed prefer the predictive aspects of the periodic system.

Davy Medal Citation

Since two eminent philosophers of science have cited the award of the Royal Society's Davy Medal to Mendeleev as evidence for the superiority of predictions in the acceptance of the periodic system, it is necessary to consider the citation of this award in full.

> The Davy Medal has been awarded to Dimitri Ivanovich Mendeleeff and Lothar Meyer.
>
> The attention of the chemists had for many years been directed to the relations between the atomic weights of the elements and their respective physical and chemical properties; and a considerable number of remarkable facts had been established by previous workers in this field of inquiry.
>
> The labors of Mendeleeff and Lothar Meyer have generalized and extended our knowledge of those relations, and have laid the foundation of a general system of classification of the elements. They arrange the elements in the empirical order of their atomic weights, beginning with the lightest and proceeding step by step to the heaviest known elementary atom. After hydrogen the first fifteen terms of this series are the following, viz.:

Lithium	7	Sodium	23
Beryllium	9.4	Magnesium	24

Boron	11	Aluminum	27.4
Carbon	12	Silicon	28
Nitrogen	14	Phosphorus	31
Oxygen	16	Sulfur	31
Fluorine	19	Chlorine	35.5
Potassium	39		

> No one who is acquainted with the most fundamental properties of these elements can fail to recognize the marvelous regularity with which the differences of property, distinguishing each of the first seven terms in the series from the next term, are reproduced in the next seven terms.
>
> Such periodic re-appearance of analogous properties in the series of elements has been graphically illustrated in a very striking manner with respect to their physical properties, such as the melting points and atomic volumes. In the curve which represents the relations of atomic volumes and atomic weights analogous elements occupy very similar positions, and the same thing holds good in a striking manner with respect to the curve representing the relations of melting-points and atomic weights.
>
> Like every great step in our knowledge of the order of nature, this periodic series not only enables us to see clearly much that we could not see before; it also raises new difficulties, and points to many problems which need investigation. It is certainly a most important extension to the science of chemistry.[48]

The first thing to emerge from an examination of this citation is that the medal is being jointly awarded to Mendeleev and Lothar Meyer. This feature has been conveniently omitted by Maher and Lipton, both of whom favor prediction over accommodation.[49] The very fact that the award is to both of these pioneers of the periodic system already argues strongly against the predictivist thesis since, according to the popular account, Mendeleev is given priority precisely because he made predictions, which were subsequently confirmed, whereas Lothar Meyer failed to make any significant predictions.

Second, the entire citation concerns the accommodation of chemical and physical phenomena of the elements and not the prediction of new elements, as Maher and Lipton's statements would seem to require. The only part of the citation that could remotely be linked with the prediction of gallium and scandium by Mendeleev is the phrase in the final paragraph that alludes to "seeing clearly much that we could not see before." However, this comment is too vague to allow such an interpretation, and even if it is a veiled reference to the prediction of the two new elements, it is clearly not stating that the medal is being awarded primarily as a result of them. So perhaps Maher and Lipton are mistaken in citing the award of the Davy Medal as an indication of the Royal Society's high regard for predictions, since the entire Davy award citation makes no mention whatsoever of the prediction of new elements.

Contemporary Reactions to the Periodic Table

Let us now examine the wider questions of how scientists at large in this period of history reacted to the introduction of Mendeleev's periodic system, and whether they regarded predictions connected with the periodic table more favorably than the accommodation of already known elements.

The second successful prediction by Mendeleev concerned the element scandium, and this case offers a good opportunity for obtaining the reactions of other scientists, since the identification of the newly discovered element was carried out by a third party, that is, neither the discoverer of the element nor Mendeleev. This third party was the French chemist Per-Teodor Clève, who wrote:

> The great interest of scandium is that its existence had been predicted. Mendeleef in his memoir on the law of periodicity, had foreseen the existence of a metal which he named ekaboron, and whose characters agree fairly well with those of scandium.[50]

Clève is clearly attaching some importance to this prediction, although there is no indication that he regards the overall case for Mendeleev's periodic system to be strengthened by this finding.

In 1879, shortly after the translation of Clève's article was published in the British journal *Chemical News*, the same journal undertook the serialization of Mendeleev's 1871 paper on the periodic law. The following interesting editorial appears along with a specially written introductory article by Mendeleev:

> Considerable attention having been drawn to M. Mendeleef's memoir "On the Periodic Law of the Chemical Elements", in consequence of the newly discovered elements gallium and scandium being apparently identical with two predicted elements ekaluminum and ekaboron, it has been thought desirable to reproduce the entire article in CHEMICAL NEWS....[51]

There followed a weekly serialization of Mendeleev's memoir in 17 parts. This may be among the strongest evidence that suggests that Mendeleev's predictions were indeed taken seriously at the time. Nevertheless, the above editorial gives no indication of whether the successful predictions did anything to enhance the status of the periodic system.

In 1881, a year after the serialization of Mendeleev's memoir appeared, the famous priority dispute between Mendeleev and Lothar Meyer broke out in the pages of the same journal, *Chemical News*. After giving precise details as to the publication of his early papers in a note to the journal, Mendeleev adds the following more general remark concerning what he believes to be the essence of the priority question:

> That person is rightly regarded as the creator of a particular scientific idea who perceives not merely its philosophical, but its real aspect, and who understands so to illustrate the matter so that everyone can become convinced of its truth. Then alone the idea, like matter, becomes indestructible.[52]

Interestingly, Mendeleev does not specifically mention any of his predictions in arguing for his priority over Lothar Meyer.[53] His note is followed by one from Lothar Meyer, in which Lothar Meyer, in turn, defends his own claim to priority with regard to the discovery of the periodic system.[54] This note is followed by a third item by the well-known organic chemist Charles-Adolphe Wurtz, who is not impressed with the periodic system at all, let alone with Mendeleev's predictions. Wurtz grants that Mendeleev's proposition is a "powerful generalization and must in future be taken into account whenever we regard the facts of chemistry from a lofty and comprehensive point of view."[55] Nevertheless, he points out that the system contains many imperfections, such as the way it reflects the then available knowledge of the rare earths. He discusses the problem with tellurium and iodine, whose atomic weight ordering is inconsistent with their chemical properties. Wurtz alludes to similar problems with cobalt and nickel, whose properties should coincide in view of their almost identical atomic weights.[56] Wurtz also points out the large chemical differences between such elements as vanadium and bromine, whose atomic weights are very closely related, which might therefore be expected to be chemically similar. He adds that the alleged gradations in properties do not in fact progress smoothly or regularly as Mendeleev would have us believe.

Wurtz then turns specifically to consider Mendeleev's predictions.

> In Mendelejeff's table we are chiefly struck with the gaps between two elements, the atomic weights of which show a greater difference than two or three units, thus marking an interruption in the progression of the atomic weights. Between zinc (64.9) and arsenic (74.9) there are two, one of which has been lately filled up by the discovery of gallium. But the considerations by which Lecoq de Boisbaudran was led in the search for gallium have nothing in common with the conception of Mendelejeff. Though gallium has filled up a gap between zinc and arsenic, and though other intervals may be filled up in future, it does not follow that the atomic weights of such new elements will be those assigned to them by this principle of classification. The atomic weight of gallium is sensibly different from that predicted by Mendelejeff. It is also possible that the future may have in reserve for us the discovery of a new element whose atomic weight will closely coincide with that of a known element, as do the atomic weights of nickel and cobalt. Such a discovery would not fill any foreseen gap. If cobalt were unknown it would not be discovered in consequence of Mendelejeff's classification.[57]

The inclusion of this rather severe criticism might be viewed as an attempt by the editor of *Chemical News* to temper his initial enthusiasm for Mendeleev's system, which had led to the 17-part serialization. Why he would otherwise choose to follow the priority dispute with this note is difficult to understand.

The fact that the successful predictions made by Mendeleev by no means gained universal acceptance for his periodic system can also be seen from further criticisms voiced by the likes of the chemist Marcellin Berthelot. In 1885, even after two of Mendeleev's predictions had been highly successful, Bertholet launched a highly critical attack on the periodic systems that had been introduced by Mendeleev and others. Not only was he unimpressed with Mendeleev's predictions, but Berthelot even refused to be seduced by the ability of the periodic system to accommodate what was already known about the elements.[58] Berthelot began by pointing out that the relations between atomic weights, atomic volumes, and physical and chemical properties had been known before the elements were placed into a periodic system. He claimed that, since these relations resulted from atomic weight relations, it was a coincidence that they reemerged when considered in the context of the periodic table. To Berthelot, this was not, therefore, proof of the existence of periodic series. He then turned to predictions and admitted that the periodic system should prove interesting in this respect. Berthelot also accepted that certain elements appeared to be missing but stressed that this was evident just from the gaps in the sequence of atomic weights. He claimed that, in their haste to fill such gaps, the authors of the periodic systems had made some mistakes, such as inserting molybdenum between scandium and tellurium.

Similarly, Berthelot mocked as "fanciful" the common grouping of hydrogen and lithium at one end of a group and copper, silver, and gold at the other end of the same group, as carried out by Mendeleev. He further accused the authors of the periodic systems of making it too elastic in admitting elements that differed by no more than two units throughout the table. He suggested that *any* future discoveries could be accommodated if this was the case. Berthelot claimed that there was no systematic means of predicting new elements from the periodic system or any means of synthetically forming the elements, thus referring to the hypothetical transmutation of the elements. Finally, Bertholet warned about the dangers of falling back into what he called a mystical enthusiasm similar to that of the alchemists.

Up to this point, Berthelot's critique seemed to have been very reasonable, but in this final remark he gave Mendeleev an easy way of responding.[59] Mendeleev took issue in particular with Berthelot's reference to a "mystic enthusiasm" and responded by accusing Berthelot of confusing the idea of the law of periodicity with the ideas of William Prout, as well as with those of the alchemists and of Democritus on primary matter. It was in response to these criticisms by Berthelot that Mendeleev also made a much quoted remark, already cited in chapter 4, in which he emphasized that the periodic system owed nothing to the idea of a "unique matter" and had no connection with the "relic of the torments of classical thought."

A look at the historical record thus reveals that the acceptance of Mendeleev's system was not a simple matter and certainly was not assured by either his accommodations or his successful predictions. Many of Mendeleev's contemporaries were impressed with the accommodations his system achieved; others, like Bertholet, seemed to not be impressed by either the predictions or the accommodations. Thus, the question remains -regarding the manner in which Mendeleev's periodic system did indeed take hold fairly quickly in the decades following its introduction and how it came to occupy the central position in chemistry it still holds today.

The Power of an Idea

Although his chemical knowledge was extensive, Mendeleev was considered to be primarily a systematizer. He produced an *idea*, the periodic system, within which chemical phenomena could be systematized. He used this idea to sort through the mass of chemical data available in his time, and though he was not always correct, he demonstrated an uncanny ability to separate valid facts from irrelevant ones. It was because he could see patterns among the properties of the elements that he was able to predict not only the existence of new elements but also their chemical and physical characteristics. The historian of chemistry William Brock has quoted Bonifatii Kedrov, the Russian historian of chemistry, as saying, "[T]he scientific world was astounded to note that Mendeleev, the theorist, had seen the properties of a new element more clearly than the chemist who had discovered it."[60] Meanwhile, the science historian Stephen Brush has posed an interesting question in asking whether theorists should be considered less trustworthy than observers. The reason one tends to give more credit to predictions than to accommodations is presumably because we suspect that a theorist might have designed his theory to fit the facts. But is it not equally possible, Brush asks, for observers to be influenced by a theory in their report of experimental facts? If so, then perhaps we should give greater consideration to observations obtained before a theory is announced than to observations produced in response to a theory.

Although Mendeleev was not above occasionally resorting to ad hoc arguments, as witnessed in his discussion of the melting point of gallium, there was nothing ad hoc about his atomic weight corrections, as unlikely as many of them may have appeared to be at the time. It is important to emphasize that there turned out to be independent empirical evidence for the new values assigned to these atomic weights. It was not that chemists simply came to accept the new values because they made elements fit Mendeleev's table better. The corrected value of the atomic weight of beryllium, for example, was confirmed independently of any consideration of its place in any table by Lars Fredrik Nilson and O. Pettersen's discovery of one of its gaseous compounds, beryllium chloride. This discovery meant that an evaluation of beryllium's atomic weight could be made using already accepted background knowledge.

In ordering the elements, Mendeleev was accommodating all that was known about them up to his time, their atomic weights, their physical properties, and their chemical character, in addition to being able to make dramatic predictions. Mendeleev did not have to correctly predict every element that would be discovered, and experimentalists were not restricted to looking only for elements that the system implied. The successful incorporation of the rare earths and the noble gases would ultimately do much to prove the validity of the periodic system. What is more, the system would be further strengthened by more general developments to come, such as the discovery of isotopes, atomic number, and later, quantum theory.

The Inert Gases

The case of the inert, or noble, gases represents an interesting counterexample to the predictivist thesis in the sense that almost nobody, including Mendeleev, had predicted or even suspected the existence of an entire family of new elements.[61] Once they had begun to be discovered, it was immediately understood that the existence of the inert gases might pose a major threat to the periodic system. Indeed, a failure to incorporate them might have led to an abandonment of the periodic system, regardless of the earlier predictive successes achieved. As it turned out, the correct placement of the noble gases did not cause any harm to the periodic system but instead did much to enhance it.

The first of the noble gases to be discovered, argon, was particularly difficult to place in the periodic system. Not only had it not been predicted from the periodic system, but there was the further difficulty that physical measurements suggested the gas was monoatomic; this was regarded with some suspicion since the only other monoatomic gas then known was vaporized mercury.

The atomicity of argon was crucial to determining its atomic weight, which in turn was essential for its accommodation into the periodic system. As Mendeleev had repeatedly stressed, atomic weight was considered to be the one essential criterion on which the periodic law was founded. Further complications regarding the atomic weight of argon arose due to doubts over the purity of the gas. There was considerable debate as to whether it consisted of a mixture of gases and whether what was being measured was actually an average atomic weight determined by the relative proportion of several components. While the interdependent issues of atomicity and the possibility of a mixture were still being discussed, a deeper and unsuspected complicating factor was operating to confuse the issue. The elements argon and the subsequent element potassium represent one of the very few examples of "pair reversals" in the periodic table.[62]

Argon was discovered in 1894 by Lord Rayleigh (John William Strutt) and William Ramsay (figure 5.2), who were studying nitrogen. Convinced by spectroscopic evidence that they had a new element on their hands, they set out to determine its properties. Because the gas was completely inert, they were forced to rely on physical measurements to determine its atomic weight. The determination of argon's specific heat was carried out through measurement of the specific heat capacities of the gas at constant pressure and at constant volume, C_p and C_v, respectively.[63]

From these measurements, Rayleigh and Ramsay could determine the ratio of translational energy to kinetic energy, which would in turn reveal the atomicity of the gas. In general, the total kinetic energy of a molecule is made up of three contributions: translational, rotational, and vibrational energy. In the case of a monoatomic system, there is only translational motion, and so kinetic energy is equal to translational energy. Rudolf Clausius had shown in 1857 that if K is the translational energy of the molecules of a gas and H is the total kinetic energy, then

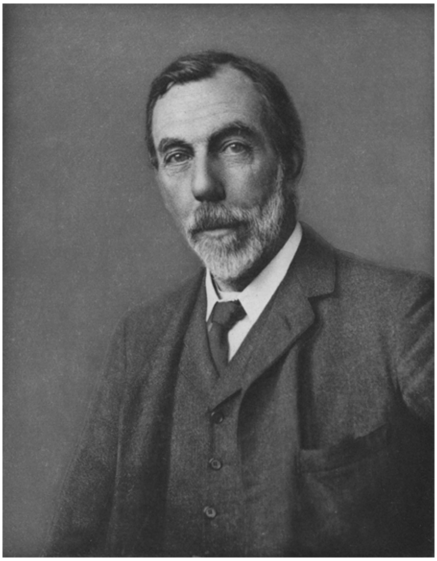


FIGURE 5.2
William Ramsay. Photo and permission from Edgar Fahs Smith Collection.

$$K/H = 3(C_p - C_v)/2C_v$$

If C_p/C_v is found to be 1.66, substitution into the equation shows that $K = H$, or in other words, all the kinetic energy of the molecules occurs in translational form. This means that the molecules are exhibiting no rotational or vibrational energy, which in turn implies the presence of an isolated atom, or monoatomicity.[64] The experimental result obtained by Rayleigh and Ramsay was that C_p/C_v was very nearly 1.66, from which they therefore inferred that argon is monoatomic. The account just given benefits from the knowledge of hindsight, since it is now well established that argon is indeed monoatomic. It took considerably more effort to arrive at this conclusion at the time when the mysterious gas was first discovered.

The public announcement of the argon problem took place on January 31, 1895, at a specially convened meeting of the Royal Society of London, and it was met with considerable debate by the leading chemists and physicists of the day. The meeting began with an exposition of the findings on the new substance given by Ramsay, including the specific heat ratio of nearly 1.66. Ramsay and Rayleigh interpreted this result to mean that the new constituent was either an element or a mixture of elements and was probably monoatomic. They admitted that the results were also consistent with diatomic or polyatomic molecules whose atoms acquire no relative motion, not even that of rotation. They added that the latter possibility seemed improbable, however, in that it would have required such a complex group of atoms to be spherical.

Rayleigh and Ramsay failed to take up a decisive position on the question of the purity of the new substance. They acknowledged that the spectral evidence provided by William Crookes, in a paper read the same evening, suggested a mixture. But they also pointed to the measurements on critical data, which indicated a sharp boiling point and melting point, as well as an observed constant pressure during boiling, all of which pointed to a single pure substance.

Their overall conclusion was that "the balance of evidence seemed to point to simplicity," meaning to a single element, but that this fact together with the probable monoatomicity suggested an atomic weight of 39.9. From this finding they were forced to conclude that such an element would find no place in the periodic table. On the other hand, Ramsay and Rayleigh proceeded to speculate that a 93.3% to 6.7% mixture of two unknown elements with atomic weights 37 and 82, one lying between chlorine and potassium and the other between bromine and rubidium, would also account for the observed density.

Henry Armstrong, the then president of the Chemical Society, politely congratulated Ramsay and Rayleigh on their researches but went on to make some criticisms. He suggested that the account of the probable nature of the new element was "of a wildly speculative character" and drew attention to the doubts expressed by Ramsay and Rayleigh over the interpretation of the specific heat data. Armstrong then proceeded to draw an analogy between nitrogen and argon. He pointed out that while nitrogen, as it occurs in the atmosphere in molecular form, is highly inert, so its constituent atoms are highly reactive. Similarly, he argued that argon, which is evidently even more inert than nitrogen, might consist of even more reactive constituent atoms. Their extreme reactivity would produce very strong interatomic bonding, thus producing a diatomic molecule so locked together that it would display translational motion without any form of relative motion between the constituent atoms.

Further support for Armstrong's view came from the Irish physicist George Fitzgerald, better known for his contributions to the theory of relativity, whose opinion had been communicated earlier in a letter to Rayleigh.[65] Like Armstrong, Fitzgerald was willing to contemplate a diatomic molecule in which the two atoms are so firmly bound together as to produce very little internal motion and added that this view would be in keeping with the chemical inertness of the new gas.

Lord Rayleigh, however, had difficulty imagining such a diatomic molecule and expressed his reservations by saying:

> That argument is no doubt perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figures roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation.[66]

William Arthur Rücker, the president of the Physical Society, pointed out that such a diatomic molecule would actually have to be spherical to produce the observed ratio of specific heats of 1.66. He acknowledged that this would represent something of a problem, but he also admitted less concern about the problem of fitting the element into the periodic table, as he did not think Mendeleev's system to be so well established that overturning it would shake the foundations of chemistry.

Finally, the chair of the meeting, Lord Kelvin, added his own comment on the issue of the specific heat ratio of 1.66, also expressing reservations about the possibility of a diatomic molecule. "I do not admit that a spherical atom could fulfill that condition," he said. "A spherical atom would not be absolutely smooth." Kelvin also disputed the notion of a rigidly connected diatomic molecule since he felt that at least some relative vibrational motion would have been detected from such a mechanical system.[67]

About two months later, a report of Mendeleev's views on the accommodation of argon appeared in *Nature*.[68] Here, Mendeleev stated that the supposition that argon is a mixture "lies beyond all probabilities." He also considered it improbable that the gas was an element due to its inert nature. He then moved on to a systematic consideration of atomic weights for the element, suggesting the following set of possible molecules:

$$A_1, A_2, A_3, \ldots A_n$$

Taking each of the possible atomicities in turn, he first discussed monoatomicity. Mendeleev was reluctant to accept the evidence for monoatomicity obtained from specific heat measurements on the grounds that there might be a chemical contribution to the kinetic energy of the molecule. He pointed to the difference between the values for C_p/C_v of 1.3 in the case of chlorine and 1.4 in the case of nitrogen, thus emphasizing the variation among diatomics and implying that even a value of 1.6, as observed in argon, might still belong to a diatomic molecule.

As might be expected, Mendeleev was most concerned with the problem of fitting the new element into his periodic system, but he dismissed monoatomicity on the grounds that there was no room in the periodic table for such an element. He reasoned that monoatomicity implied an atomic weight for argon falling between chlorine and potassium and that this would imply "an eighth group in the third series," something that he found inadmissible. This is a surprising error on the part of the master chemist, since there is in fact no fundamental reason why an eighth group should not be introduced. In fact, this is precisely how the problem was solved in due course.

Mendeleev raised similar objections against the notion of a diatomic argon molecule. Continuing with his original list of possible atomicities, he then settled on triatomicity, concluding that argon was nothing but a triatomic form of nitrogen and not a new element after all:

> If we suppose further that the molecule of argon contains three atoms, its atomic weight would be about 14, and in such case we might consider argon as condensed nitrogen N_3. There is much to be said in favour of this last hypothesis....[69]

Among the reasons for favoring this molecule, Mendeleev argued that it would account for the "concurrent existence of nitrogen and argon in nature" and similarly that the inertness of argon might be related to the fact that it is derived from nitrogen. Molecules with higher atomicities, namely, 4 and 5, were ruled out because they would require atomic weights of 10 and 8, respectively, and could not thus be accommodated into the periodic system. As for hexatomicity, Mendeleev considered this plausible and indeed thought it to be the second most likely atomicity after triatomic N_3.

Meanwhile, the debate had spread to the larger scientific community. John Hall Gladstone, one of the pioneers of the relationship between refractive index and molecular structure, gave five reasons why an element with an atomic weight of 20 would fail to fit into the periodic system. He then gave a further five reasons why he considered an element of atomic weight 40 would be well accommodated into the periodic table. One cannot help concluding that Gladstone was wrong on a total of 10 counts!

Within two years, terrestrial helium had been discovered, and the problem became one of accommodating two elements, namely, argon and helium. A further three years were to pass before the discovery of krypton, neon, and xenon. A whole new family of elements had been discovered without having been generally predicted, and the accommodation of these new elements into the periodic table was proving to be far from trivial. Indeed, it presented a severe threat to the survival of Mendeleev's system.

Mendeleev visited London in late 1895 and discussed the argon problem with Ramsay. He reported back to the Russian Physico-Chemical Society on his return to Moscow: "The subject has progressed little. There is little for its solution and the matter seems particularly obscure."[70] Two years later, he wrote that since no compounds could be formed from argon and helium, their atomic weights should be regarded as doubtful. For Mendeleev, the study of compounds played an essential role in the incorporation of elements into the periodic system. He was reluctant to accept argon and helium as new elements, as he would not entertain the possibility that an element could be completely inert.[71]

Finally, in the spring of 1900, at a meeting in Berlin, Ramsay suggested to Mendeleev that argon and its analogues should be placed in a new group between the halogens and the alkali metals. They would thus appear at the right-hand edge of the table and would serve to extend the length of each period by one element.[72] In spite of all his previous views on the inert gases, Mendeleev received this suggestion favorably and wrote of his response in 1902: "This was extremely important for him [Ramsay] as an affirmation of the position of the newly discovered elements, and for me as a glorious confirmation of the general applicability of the periodic law."[73] Mendeleev also adds that this step represented the "magnificent survival" of the periodic system in what had been a "critical test." Indeed, the periodic system had come through this test with "flying colors." Could it be that the eventual successful incorporation of the noble gases into the periodic table counted as much in favor of the periodic system's acceptance as Mendeleev's celebrated predictions? My own belief is that it did, as did the eventual successful incorporation of the rare earth elements.

Conclusion

The claim is sometimes made that successful prediction gives more credit to a theory than does the accommodation of known facts. But it is difficult to find clear-cut evidence for this claim in the technical writings of scientists.[74] A successful prediction may yield much favorable publicity for a theory and thereby force other scientists to give it serious consideration. But subsequent evaluations of the theory in the scientific literature usually do not give greater weight to the prediction of novel facts than to the persuasive deductions of known facts.

This may be what happened with Mendeleev's periodic system. It was announced in 1869 to mixed reviews but seems to have received more favorable attention after the discovery of gallium in 1875. Rather than confirming that prediction of new elements was the overwhelming factor in the eventual acceptance of the system, the discovery of gallium, scandium, and germanium may have served simply to bring the system to the attention of the scientific community. From there, it appears that its many strengths began to be appreciated. In addition to the prediction of new elements, Mendeleev successfully predicted the correct atomic weights of many already existing elements, and these successes would have contributed to the acceptance of his periodic system.

But the placement of difficult elements such as beryllium, the accommodation of the newly discovered noble gases, and the ongoing struggle to position the rare earths all contributed to an atmosphere of productive debate that surrounded the periodic system. These factors may well have contributed just as much as the predictions to the eventual acceptance of the system, contrary to the popular myth that assigns the greatest credit to Mendeleev almost exclusively on the basis of his successful predictions. By 1890, Mendeleev's system was a permanent fixture on the landscape of chemistry. Almost all the lacunae of the magnificent edifice had been explored, revealing its profound elegance and propelling the research agenda for chemistry, and even physics, into the next century.

Notes

1. An edited collection of articles that examines the early acceptance of the periodic system in Russia, Germany, Britain, France, the Czech lands, Sweden, Denmark, Norway, Spain, Portugal, Italy and Japan is M. Kaji, H. Kragh, G. Pallo (eds.), *Early Responses to the Periodic System*, Oxford University Press, New York, 2015.

2. As previously mentioned, Mendeleev was not, in fact, the first to predict unknown elements. William Odling, John Newlands, and Julius Lothar Meyer all did so before him. E.g., Newlands left spaces for yttrium, indium, and germanium. For germanium, he predicted an atomic weight of 73, which compares very favorably with the current value of 72.59.

3. W. Brock, *The Norton History of Chemistry*, Norton, New York, 1992, pp. 324–325.

4. For general references to the prediction/accommodation debate, see chapter 2, note 73

5. S.G. Brush, The Reception of Mendeleev's Periodic Law in America and Britain, *Isis*, 87, 595–628, 1996.

6. Posing such questions is complicated by the fact that, in some cases, the successful accommodation of an element relied on Mendeleev's correction of the atomic weights of some elements.

7. None of these comments should be taken to contradict what has already been said regarding Mendeleev.

8. These days, chemists can be associated with a single element. When I taught chemistry at Purdue University, I worked in the Brown Building, named after H.C. Brown, who won a Nobel Prize in 1979 for his pioneering work in boron chemistry, which he continued to do until his death in December 2004 (at age 92). Similarly, the chair of chemistry during my days at Purdue was Richard Walton, who is the world's expert on the chemistry of rhenium. Few people, if any, are still considered experts on the chemistry of all the elements.

9. The myths are explored and debunked in some detail in M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004.

10. This is not to say that chemical aspects were absent from Lothar Meyer's system. E.g., the headings for the various groups in his system consisted of different valences, as mentioned in chapter 3.

11. Not to be confused with group VIII in the modern table, the noble gases, which had not yet been proposed when Mendeleev discovered his periodic system. It was these elements, e.g., iron, cobalt, and nickel, that were termed transition metals in the sense of providing a transition between successive periods in the short-form table.

12. These elements were originally called the transition elements, whereas the term has now come to mean the elements in the central block of the medium-long form table as well as the elements placed under the table as a footnote. In modern terminology, these elements form the d- and f-blocks, respectively.

13. He may have reached this conclusion after seeing Lothar Meyer's published system of 1870, which already incorporated this improvement.

14. In fact, uranium is now known to form compounds with hydrogen, although they tend to be nonstoichiometric, their formulas being written as UH_x, where x varies.

15. As is the case of Mendeleev's claimed interpolations to obtain the atomic weights of gallium, scandium, and germanium, his predicted values were not exactly as prescribed in his explanations.

16. Unlike in chapter 2, where the original version was given, relative to the O = 1 standard, the form given here is the more common one based on O = 16, hence, the difference in the constant cited in each chapter.

17. L.F. Nilson, O. Petterson, *Berichte*, 11, 381–386, 1878.

18. T.S. Humpidge, On the Atomic Weight of Glucinum (Beryllium) [Abstract], *Proceedings of the Royal Society*, 38, 188–191, 1884; Humpidge, On the Atomic Weight of Glucinum (Beryllium) Second Paper, *Proceedings of the Royal Society*, 39, 1–19, 1885.

19. More generally, the change in valence across the second and third periods shows a smooth increase from 1 to 4, followed by an equally uniform decrease down to 0 for the noble gases.

20. In 1946, Seaborg discovered that a major change was needed in the periodic table. Several elements that had been regarded as belonging to a fourth transition metal series were separated out from the main body of the periodic table to form the lanthanide and actinide series. Uranium is among these elements and is no longer regarded as a transition metal.

21. The prefix "eka-" is Sanskrit for the numeral one. Mendeleev also used "dvi-," or two, on some occasions to describe a second element that was like a particular known element, or a double of it.

22. Once again, this irregularity occurs because many elements consist of mixtures of various isotopes, and their atomic weights are thus averages of their values.

23. D.I. Mendeleev, Über die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente, *Zeitschrift für Chemie*, 12, 405–406, 1869, quoted from p. 406.

24. Ibid., p. 42, note 16.

25. Strictly speaking, these provisional names were coined in the following year of 1871.

26. I thank Michael Gordin for this information. The article is D.I. Mendeleev, Die periodische Gessetzmässingkeit der chemischen Elements, *Annalen der Chemie und Pharmacie*, 8, 133–229, 1871.

27. The first person to present such tables of comparison for Mendeleev's predictions was Pierre Clève.

28. P. E. Lecoq De Boisbaudran, Charactères Chimiques et Spectroscopiques d'un Nouveau Métal, le Gallium, Decouvert Dans un Blende de la Mine de Pierrefitte, Valée d'Argèles (Pyrénées), *Comptes Rendus de l'Académie des Sciences, Paris*, 81, 493–495, 1875.

29. De Boisbaudran originally stated that the density of the element was 4.7 g/cm^3. Mendeleev had predicted a value of 5.9 g/cm^3 and wrote to De Boisbaudran, asking him to redetermine the value, which he did, obtaining a value close to the present value of 5.904 g/cm^3.

30. Others maintain that he was really naming the element after himself in view of "Lecoq" contained in his own name. The Latin for cock is *gallus*.

31. D.I. Mendeleev, Remarques à Propos de la Découverte du Gallium, *Comptes Rendus de l'Académie des Sciences, Paris*, 81, 969–972, 1876.

32. D. Mendeleev, La Loi Périodique des Éléments Chimiques, *Moniteure Scientifique*, 21, 691–735, quoted from p. 692.

33. D.I. Mendeleev, The Periodic Law of the Chemical Elements, *Journal of the Chemical Society*, 55, 634–656, 1889.

34. The optical ether was a medium that had been invoked as the carrier of the electromagnetic force, although it had never been detected experimentally. Nevertheless, this concept served a mathematical purpose in the theory of electromagnetism until it was conclusively refuted by Albert Einstein's 1905 theory of special relativity.

35. Since the present book is primarily about the development of the periodic system and not about Mendeleev, very little has been said on the latter's view on the ether. Mendeleev's interest in this issue began early on in his career and was the motivation for his work on deviations from the gas laws carried out in the 1870s. Although he failed to uncover any evidence for the ether, he maintained a theoretical interest in it, which formed the basis for his speculations aimed at counteracting the discoveries of radioactivity and transmutation, which Mendeleev remained opposed to almost until his death in 1907. More information on Mendeleev and the ether can be found in Gordin's book, *A Well-Ordered Thing,* Basic Books, New York, 2004. A revised edition was published in 2019.

36. D.C. Rawson, The Process of Discovery: Mendeleef and the Periodic Law, *Annals of Science*, 31, 181–204, 1974.

37. D.I. Mendeleev, *Perioicheskii Zakon. Osnovye Stat'I, Compilation and Commentary of Articles on the Periodic Law*, by B.M. Kedrov, Klassiki Nauk, Soyuz sovietskikh sotsial'sticheskikh respublik, Leningrad, 1958, p. 316, note 16 (emphasis added).

38. For fuller details of Mendeleev on magnesium and beryllium, see J.R. Smith, *Persistence and Periodicity*, unpublished Ph.D. thesis, University of London, 1975.

39. J. van Spronsen, *The Periodic System of the Chemical Elements, the First One Hundred Years*, Elsevier, Amsterdam, 1969, p. 215.

40. Although it must be acknowledged that the dramatic successes came first.

41. A similar table, though containing far fewer entries and only Mendeleev's later predictions, is given by W. Brock, *The Norton History of Chemistry*, Norton, New York, 1992, p. 325. It is interesting to also note this author's remark: "[H]is predictions of eka-manganese, tri-manganese, dvi-tellurium, dvi-caesium and eka-tantalum were fortuitous guesses rather than predictions based upon a firm and accurate placing of their homologues in the table."

42. My count of Mendeleev's successes and failures has been challenged in P. Stewart, Mendeleev's predictions: success and failure, *Foundations of Chemistry*. 21, 3–9, 2019.

43. Entry under a section entitled Chemical Notices from Foreign Sources, *Chemical News*, 23, 1871, p. 252, mentioning Mendeleev's paper published in German in *Berichte der Deutschen Chemischen Gesellschaft zu Berlin*, 6, 1871.

44. P. Lipton, Prediction and Prejudice, *International Studies in Philosophy of Science*, 4, 51–60, 1990.

45. P. Lipton, *Inference to the Best Explanation*, Routledge, London, 1991.

46. See Lipton, Prediction and Prejudice, *International Studies in Philosophy of Science,* 4, 51–60, 1990.

47. Contemporary historians have begun to redress this imbalance. For example, S.J. Brush, The Reception of Mendeleev's Periodic Law in America and Britain, *Isis*, 87, 595–628, 1996.

48. W. Spottiswode, President's Address, *Proceedings of Royal Society of London*, 34, 303–329, 1883, quoted from p. 392.

49. On this issue, unlike the alleged time lag, as I have called it, Maher cannot be exonerated on the basis of any mistake reported by his cited source on the history of chemistry, namely, the book by Ihde, since the latter does not mention the award of the Davy Medal. A.J. Ihde, *The Development of Modern Chemistry*, Dover Publications, New York, 1984, as cited in chapter 6, note 37.

50. P.T. Clève, Sur le Scandium, *Comptes Rendus des Seances de l'Académie des Sciences*, 89, 419–422, 1879, quoted from p. 421.

51. Editorial by W. Crookes, *Chemical News*, 1879.

52. D.I. Mendeleev, On the History of the Periodic Law, *Chemical News*, 43, 15, 1881.

53. Nevertheless, I note that Gordin argues that Mendeleev regarded predictions very seriously. M. Gordin, *A Well-Ordered Thing*, Basic Books, New York, 2004.

54. For a recent reassessment of this priority debate, see M. Gordin, The Textbook Case of a Priority Dispute: D. I. Mendeleev, Lothar Meyer, and the Periodic System, in M. Biagioli, J. Riskin (eds.), *Nature Engaged*, Palgrave Studies in Cultural and Intellectual History, Palgrave Macmillan, New York, 2012.

55. A. Wurtz, *The Atomic Theory*, translated by E. Cleminshaw, Appleton, New York, 1881.

56. This latter turned out to be another case of "pair reversal."

57. A. Wurtz, *The Atomic Theory*, translated by E. Cleminshaw, Appleton, New York, 1881, p. 16.

58. Marcellin Berthelot, *Les Origines de L'Alchemie*, Steinheil, Paris, 1885, p. 311.

59. D. Mendeleev, The Periodic Law of the Chemical Elements, *Journal of the Chemical Society*, 55, 634–656, 1889. This is Mendeleev's Faraday lecture. See the comments on p. 644.

60. W. Brock, *The Norton History of Chemistry*, Norton, New York, 1992, pp. 324–325.

61. But to be more accurate, at least two authors, William Sedgwick and Jörgen Thomsen, had independently predicted the possibility of a group of completely unreactive elements.

W. Sedgwick, The Existence of an Atom Without Valency of the Atomic Weight of "Argon" Anticipated Before the Discovery of "Argon" by Lord Rayleigh and Prof. Ramsay, *Chemical News*, 71, 139–140, 1895; J. Thomsen, *Anorganische Chemie*, 9, 282, 1895. A recent scientific biography of Thomsen is, H. Kragh, *Julius Thomsen. A Life in Chemistry and Beyond*, Royal Danish Academy of Sciences and Letters, 2016. In addition the noble gases were predicted by Le Coq de Boisbaudran and an amateur American scientist, J.C. Reed.

62. Recall that at the time the argon problem arose only one pair reversal had yet come to light, that of iodine and tellurium, and that its explanation would not be obtained until nearly 20 years later with the discovery of isotopes and the work of Henry Moseley.

63. W. Ramsay and Lord Rayleigh, Argon a New Constituent of the Atmosphere, *Chemical News*, 71(1836), 51–63, 1895.

64. Since rotational motion can occur only about the common center of mass of a polyatomic system, its absence is an indication that the molecules in the gas are not polyatomic. Isolated atoms are perfectly spherical, so any rotational motion they might exhibit is undetectable. Similarly, vibrational motion can exist only between any two or more atoms in a polyatomic molecule, so its absence would also accord with monoatomicity.

65. This is the same Fitzgerald who anticipated, to some extent, Einstein's special relativistic length contraction.

66. W. Ramsay and Lord Rayleigh, Argon a New Constituent of the Atmosphere, *Chemical News*, 71, 51–63, 1895, quoted from p. 62.

67. Lord Kelvin, *Chemical News*, Argon a New Constituent of the Atmosphere *Chemical News*, 71, 51–63, 1895, quoted from p. 63.

68. Professor Mendeleev on Argon (Report of the Russian Chemical Society Meeting), March 14, 1895, *Nature*, 51, 543, 1895.

69. Ibid.

70. As cited by J.R. Smith, *Persistence and Periodicity*, unpublished Ph.D. thesis, University of London, 1975, p. 456.

71. It has since been discovered, in work beginning in the 1960s, that the noble gases do in fact form stable compounds, with the exception of helium and neon, which still appear to be unreactive.

72. It should be remembered that even Newlands had anticipated this possibility, which would in no way destroy the periodicity of the remaining elements in the table.

73. As cited by J.R. Smith, *Persistence and Periodicity*, unpublished Ph.D. thesis, University of London, 1975, p. 460. Also see D. Mendeleev, *An Attempt Towards a Chemical Conception of the Ether*, Longmans, Green and Co., London, 1904, p. 21.

74. S.J. Brush, Prediction and Theory Evaluation, *Science*, 246, 1124–1129, 1989.

CHAPTER 6

The Nucleus and the Periodic Table

Radioactivity, Atomic Number, and Isotopy

Theories of the atom were reintroduced into science by John Dalton and were taken up and debated by chemists in the nineteenth century. As noted in preceding chapters, atomic weights and equivalent weights were determined and began to influence attempts to classify the elements. Many physicists were at first reluctant to accept the notion of atoms, with the tragic exception of Ludwig Boltzmann, who came under such harsh criticism for his support of atomism that he eventually took his own life.[1] But around the turn of the twentieth century, the tide began to turn, and physicists not only adopted the atom but transformed the whole of science by performing numerous experiments aimed at probing its structure. Their work had a profound influence on chemistry and, more specifically for our interests here, the explanation and presentation of the periodic table.

Beginning with J.J. Thomson's discovery of the electron in 1897, developments came quickly.[2] In 1911, Ernest Rutherford proposed the nuclear structure of the atom, and by 1920 he had named the proton and the neutron. All of this work was made possible by the discovery of X-rays in 1895, which allowed physicists to probe the atom, and by the discovery of radioactivity in 1896. The phenomenon of radioactivity destroyed the ancient concept of the immutability of the atom once and for all and demonstrated that one element could be transformed into another, thus in a sense achieving the goal that the alchemists had sought in vain.

The discovery of radioactivity led to the eventual realization that the atom, which took its name from the idea that it was indivisible, could in fact be subdivided into more basic particles: the proton, neutron, and electron. Rutherford was the first to try to "split the atom," something he achieved by using one of the newly discovered products of radioactive decay, the alpha particle.

In addition to its well-known medical applications, the earlier discovery of X-rays was to provide a powerful tool that could be used to study the inner structure of matter. By using these rays, Henry Moseley later discovered that a better ordering principle for the periodic system is atomic number rather than atomic weight. He did this by subjecting samples of many different elements to bombardment with X-radiation.

The dual discoveries of radioactivity and X-rays made possible the further discovery and identification of several new elements, such as radium and polonium, which needed to be accommodated, and thus provided further tests of the robustness of the periodic system and its ability to adapt to changes. Indeed, while it is the electron that is mainly responsible for the chemical properties of the elements, discoveries connected with the nucleus of the atom nevertheless have had a profound influence on the evolution of the periodic system. The exploration of the nucleus, along with further work on the nature of X-rays and radioactivity, led to the discovery of atomic number and isotopy, two developments that would together resolve many of the lingering uncertainties surrounding Dmitri Mendeleev's periodic system.

The discovery of isotopy initially presented certain dangers for the periodic system. The large number of new isotopes that were discovered suggested that there were many more "atoms," in the sense of smallest possible particles, of any particular element than had previously been recognized. Some chemists even suggested that the periodic table would have to be abandoned in favor of a classification system that included a separate place for every single isotope. Luckily, this idea was resisted since, as it turned out, isotopes of the same element showed identical chemical properties.[3]

The discovery of atomic number provided one of the most clear-cut modifications the periodic system had undergone since its foundation had been laid by the likes of Johann Döbereiner some 100 years previously. When the concept of atomic number was combined with the new understanding of isotopy, it became possible to appreciate why William Prout's hypothesis (that all elements are composites of hydrogen) had been so tantalizing to the early pioneers of the periodic system. Indeed, Prout's hypothesis could now be said to be valid in the somewhat modified form that all atoms in the periodic table were multiples of a single unit of atomic number or, as it was subsequently named, the proton. It also became possible to explain why triads had been so enticing and so instrumental in the early evolution of the periodic system.

The four main discoveries of X-rays, radioactivity, atomic number, and isotopy are examined in this chapter by following a roughly historical order, although it must be appreciated that there was much overlap among these four themes.

X-Rays and Becquerel Rays

> By the beginning of 1895 Röntgen had written forty-eight papers now practically forgotten. With his forty-ninth he struck gold.
>
> Emilio Segrè, *From X-rays to Quarks*

This is how the Italian-born physicist Emilio Segrè described the career of Wilhelm Conrad Röntgen before his momentous discovery of X-rays.

On November 8, 1895, Röntgen, a German physics professor, was working in his darkened laboratory in Würzburg. His experiments focused on passing an electrical current into highly evacuated glass tubes known as Crookes tubes. To Röntgen's surprise, he noted that when one of his tubes was charged, an object across the room began to glow. This proved to be a barium platinocyanide-coated screen too far away to be reacting to the cathode rays coming from the tube. Over the next few days, Röntgen experimented in various ways with what he began to suspect might be a new form of emanation. Quite by accident, while holding materials between the tube and screen to test the new rays, he saw the bones of his hand clearly displayed on the screen in an outline of flesh. This was the first time anyone had ever seen a medical X-ray image. Röntgen plunged into seven weeks of intense and secretive experimentation in order to determine the nature of the mysterious rays. He worked in isolation, telling a friend that he had discovered something interesting but that he did not know whether his observations were correct.

On December 28, 1895, Röntgen gave his preliminary report to the president of the Würzburg Physical-Medical Society, accompanied by experimental radiographs, including an image of his wife's hand, which survives to this day. A few days later, he sent printed reports to physicist friends across Europe, and by January the world had been gripped by "X-ray mania." Röntgen was acclaimed as the discoverer of a medical miracle, and although he accepted the first Nobel Prize in physics in 1901, he decided not to seek patents or proprietary claims on X-rays.

One of the many scientists to whom Röntgen sent his X-ray images was Henri Poincaré, who in turn showed one of these radiographs to his colleagues at the Académie des Sciences in Paris, on January 20, 1896. Henri Becquerel, a professor at the Musée d'Histoire Naturelle and member of the academy, took note of a remark by Poincaré on the possible link between X-rays and luminescence. On returning to his laboratory, Becquerel designed an experiment to test the hypothesis that X-ray emission and luminescence are related. In order to see if a phosphorescent body emitted X-rays, he chose a hydrated salt of uranium that he had prepared some years before. On February 20, Becquerel placed a transparent crystal of the salt on a photographic plate wrapped between two thick sheets of black paper, and the experimental setup was exposed to sunlight for several hours. After development, the silhouette of the crystal appeared in black on the photograph, and Becquerel concluded that the phosphorescent substance emitted a penetrating radiation able to pass through black paper.

Unable to repeat such experiments in the following days because of a lack of sunshine, Becquerel put away his salt crystal, placing it by chance on an undeveloped photographic plate in a drawer. Later he developed the plate in order to determine the amount by which the phosphorescence had decreased. To his great surprise, he found that the phosphorescence had not decreased at all but was more intense than it had been on the first day. Noticing a shadow on the plate made by a piece of metal he had placed between it and the salt, Becquerel realized that the salt's activity had continued in the darkness. Clearly, sunlight had been unnecessary for the emission of the penetrating rays. Could it be that just one year after the discovery of X-rays, another new form of emanation was beginning to reveal itself?

Becquerel also found that the activity of his uranium salt did not diminish with time, even after several months. He also tried to use a nonphosphorescent uranium salt and found that the new effect persisted. He soon concluded that the emanation was due to the element uranium itself. Even after about a year had passed, from when he first began his experiments, the intensity of the new rays had shown no signs of decreasing. But Becquerel was soon to move onto other scientific interests, and it was left to others to explore the rays in greater detail.[4]

Radioactivity

The Polish born chemist-physicist Marie Curie (figure 6.1), neé Sklodowska, was the first to take up the study of Becquerel rays.[5] For her doctoral project, Marie Curie began to explore whether elements other than uranium might also produce Becquerel rays. She found that thorium, which occurs two places before uranium in the periodic table, also shows this form of behavior; she coined the term "radioactivity" to describe this new property of matter.

While experimenting with pitchblende, an ore of uranium, Curie found that this material exhibited a more intense level of radioactivity than did pure uranium,

FIGURE 6.1
Marie Curie. Photo and permission from Emilio Segrè Collection.

which itself showed greater radioactivity than did uranium salts. She made the obvious deduction that a new element might be present in pitchblende and, working in 1898 with her husband, Pierre Curie, quickly succeeded in extracting a substance with 400 times the activity of uranium, which she named polonium after her native country. This element would find its place at the foot of group VI of the periodic table, below selenium and tellurium and eight places before uranium.

Continuing to work with the pitchblende they had used to extract polonium, the Curies found that it showed traces of yet another substance, which, after much separation and purification, displayed an even more pronounced level of radioactivity, amounting to about 900 times that of uranium. This element, also discovered in 1898, was named radium.

Meanwhile, other physicists were also exploring Becquerel's rays. After studying in Cambridge under Thomson, the New Zealand-born physicist Ernest Rutherford moved to McGill University in Montreal. There he undertook a line of inquiry connected with Becquerel's rays by investigating the nature of the radiation itself. In 1899, he showed that radioactivity, as displayed by uranium, for example, produced a species of rays that could easily be absorbed by a thin metallic surface. He called them alpha rays. He also discovered a more penetrating species of rays, which he termed beta rays. Rutherford's identification of alpha rays, which, as he eventually realized, consisted of atoms of helium stripped of its two electrons, was to provide a powerful tool for probing the structure of the atom.

Between the years 1900 and 1903, Rutherford began to study the chemistry of radioactive substances. Working with a young colleague, the chemist Frederick Soddy (who will be featured prominently later in this chapter), he made an epochal discovery, remarkable especially for its impact on understanding of the nature of the chemical elements. Rutherford and Soddy were compelled to announce that, in the course of radioactive reactions, certain elements were transformed into completely new elements. While fully aware of the possible criticism that such a notion might bring, they went as far as to describe this new phenomenon as chemical transmutation, thus evoking the age-old dream of the alchemists.

Some authors believe that the interpretation of the properties of the elements passed from chemistry to physics as a result of the discovery of radioactivity. They speak of "the redefinition of Mendeleev's chemical element, which would lead to its appropriation by physics."[6] I believe this view to be overly reductionistic, as presumably did Fritz Paneth, who formulated his "intermediate position" in order to uphold the integrity of the chemical view of the elements and of the periodic system.[7]

The Discovery of the Nucleus

In 1911, following some experiments by his students Hans Geiger and Ernest Marsden, Rutherford revived the notion of a planetary atom in which electrons were believed to circulate around a central nucleus. As discussed in chapter 7, Jean Perrin and, in a somewhat different version, Hantaro Nagaoka were the first to propose such atomic models.[8] But the nuclear atom had since been eclipsed by the work of Thomson, which had suggested that the electrons were embedded in the main body of the atom.

Upon firing a stream of positively charged alpha particles at a thin foil made of gold, Geiger and Marsden observed that some of the particles were scattered at very large angles and some even appeared to rebound straight back toward the incoming direction. Such a set of findings was inexplicable in terms of Thomson's model, in which the positive charge of the atom was diffused throughout the atom. This model predicted that almost all of the alpha particles would pass through the foil. Rutherford was forced to conclude that the atoms in the foil must contain concentrations of positive charge intense enough to deflect some of the alpha particles. He thus discovered that the positive charge is localized in a very small volume at the center of the atom, while the negative charge is diffused throughout the entire volume.

On the basis of his analysis of Geiger and Marsden's alpha-scattering experiments, Rutherford further concluded that the charge on an atom is approximately half of its atomic weight. Rutherford and his colleagues observed that the degree of scattering is proportional to the square of the atomic weight of any particular atom. This effect was checked in a number of different target elements ranging from aluminum to lead. This, in turn, led to the conclusion that the scattering was proportional to the square of the nuclear charge, given that it is charge, rather than weight, that causes scattering of charged alpha particles. From further analysis of the scattering data, Geiger and Marsden arrived at the following approximate relationship between charge (Z) and atomic weight (A):

$$Z \approx A/2$$

Another British physicist, Charles Barkla, had arrived at precisely the same conclusion, also in 1911, by analyzing the scattering of X-rays from various substances. Barkla found that heavier elements produced a greater scattering in amounts proportional to their atomic weights and concluded that "the number of scattering electrons per atom is about half the atomic weight in the case of the light atoms."[9] Since in the case of neutral atoms the number of positive charges is equal to the number of electrons, the conclusions of Rutherford and Barkla are identical.

Atomic Number

Rutherford's and Barkla's work on atomic charge contributed to the discovery of atomic number, but it was not the main evidence that brought it to the foreground. The discovery of atomic number provides the opportunity for a little digression on how the history of science is frequently rewritten and sanitized by subsequent commentators. The real discoverer of atomic number was the amateur scientist Anton van den Broek (figure 6.2), whose contributions tend to be neglected. It is often thought that van den Broek merely summarized the work of physicists Rutherford and Barkla, but the true story is altogether different. It was van den Broek's close study of Mendeleev's periodic table, and his prolonged attempts to improve upon it, that led to his discovery of an ordinal number associated with each element. It also led to the identification of this number with the nuclear charge as well as the number of electrons in any atom.

Van den Broek trained in law and econometrics but published a number of influential articles in the leading scientific journals of his day. His first paper appeared in 1907 under the title "The α particle and the Periodic System of the Elements."[10] It took as its point of departure a paper of the previous year in which Rutherford had suggested various explanations for the nature of the α particle. One of these suggestions, and the one favored by van den Broek, was that this particle consisted of half of a helium atom with a charge of +1.[11] Van den Broek gave the name of alphon to this particle and proposed that it might take the place of the hydrogen atom in Prout's theory that all elements are composites of one basic particle.

According to van den Broek's scheme, each particular number of aggregated alphons would thus correspond to a particular chemical element. Since the weight of the helium atom was known to be four units, the alphon would have a weight of 2, and all even numbers of composite alphons would correspond to the weights of the known elements. An atom of uranium, for example, with an atomic weight

FIGURE 6.2
Anton van den Broek. Photo and permission from Jan van Spronsen.

of 240, would be composed of 120 alphons, and so on. Since atomic weights are not exact multiples of each other, van den Broek realized that this suggestion would not be precise, but in the Pythagorean spirit of previous Proutian speculations, he was not unduly concerned by this aspect.

Of course, such a system required many more elements than were known to exist at the time if there were to be a total of 120, ending with uranium, which was the heaviest known element. Van den Broek made up for part of this deficit by incorporating many of the new radio-elements that had recently been discovered. These species would turn out to be isotopes rather than genuine new elements, but to enter into such matters now would be to get ahead of the story. At the time, the work on radioactivity that was emerging gave van den Broek confidence that the gaps in his table would be filled. In addition, the question of how to accommodate the rare earth elements into the periodic system had still not been settled, and it seemed plausible that several new rare earth elements awaited discovery.

In his paper of 1907, van den Broek included a periodic table constructed according to his scheme, showing a total of 41 gaps representing undiscovered elements that would have to be filled between hydrogen and uranium (figure 6.3). Each even number in the table corresponds to a chemical element, and the difference in atomic weight between any two adjacent elements is two units.

In 1911, van den Broek published a second paper, in which he claimed that Mendeleev had not sufficiently satisfied the requirements of chemical periodicity of the elements.[12] He also noted that Mendeleev had intended to devise a three-dimensional periodic system, which would have remedied the situation, and it was

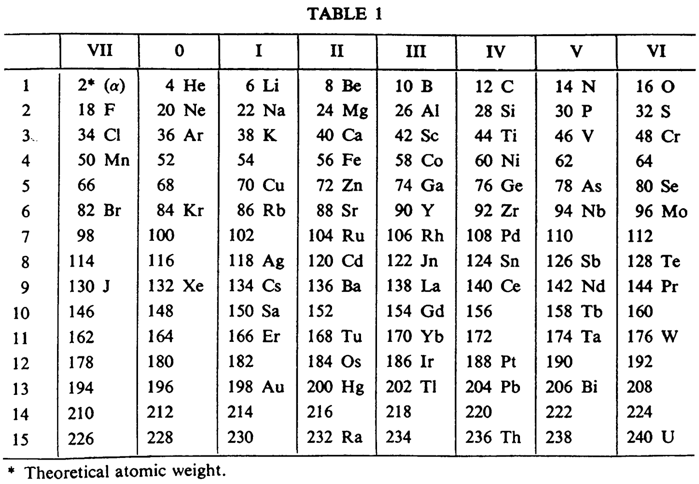


TABLE 1

	VII	0	I	II	III	IV	V	VI
1	2* (α)	4 He	6 Li	8 Be	10 B	12 C	14 N	16 O
2	18 F	20 Ne	22 Na	24 Mg	26 Al	28 Si	30 P	32 S
3	34 Cl	36 Ar	38 K	40 Ca	42 Sc	44 Ti	46 V	48 Cr
4	50 Mn	52	54	56 Fe	58 Co	60 Ni	62	64
5	66	68	70 Cu	72 Zn	74 Ga	76 Ge	78 As	80 Se
6	82 Br	84 Kr	86 Rb	88 Sr	90 Y	92 Zr	94 Nb	96 Mo
7	98	100	102	104 Ru	106 Rh	108 Pd	110	112
8	114	116	118 Ag	120 Cd	122 Jn	124 Sn	126 Sb	128 Te
9	130 J	132 Xe	134 Cs	136 Ba	138 La	140 Ce	142 Nd	144 Pr
10	146	148	150 Sa	152	154 Gd	156	158 Tb	160
11	162	164	166 Er	168 Tu	170 Yb	172	174 Ta	176 W
12	178	180	182	184 Os	186 Ir	188 Pt	190	192
13	194	196	198 Au	200 Hg	202 Tl	204 Pb	206 Bi	208
14	210	212	214	216	218	220	222	224
15	226	228	230	232 Ra	234	236 Th	238	240 U

* Theoretical atomic weight.

FIGURE 6.3 Van den Broek table of 1907. The α Particle and the Periodic System of the Elements, *Annalen der Physik*, 23, 199–203, 1907, p. 201. This version is from T. Hirosige, The Van den Broek Hypothesis, *Japanese Studies in the History of Science*, 10, 143-162, 1971. p. 148, (by permission from the publisher).

this task that van den Broek was proposing to take up now. Despite this assertion, the table that van den Broek published in this paper was in fact two dimensional, although he implied that it could be constructed in three dimensions (figure 6.4). The third dimension would consist of a short series of three elements, each of which is shown diagonally on the two-dimensional table. In any case, none of the conclusions that van den Broek drew from this new table depended on its supposed three-dimensional nature.

In the 1911 article, the notion of the alphon had disappeared, but van den Broek retained the idea of successive elements differing by two units of weight, whereas in Mendeleev's table successive elements typically showed alternating mean differences of approximately two and four units.

That same year, van den Broek also published a very brief, 20-line letter to *Nature* magazine.[13] This letter may represent the first anticipation of the concept of atomic number, given that John Newlands's much earlier suggestion of an ordinal number for each of the elements (see chapter 3) was rather more tenuous. Van den Broek began by drawing attention to the fact that two lines of experimental research, namely, Rutherford's and Barkla's, supported the view that the charge on an atom is approximately half its atomic weight, or to repeat an equation that appeared just above, $Z \approx A/2$. This evidence had provided support for his speculation of 1907 that atomic weight increases by approximately two units between each two consecutive elements.[14] Van den Broek then referred to his new periodic table and his prediction that 120 elements exist altogether, ending with the words:

TABLE 2

		0			I			II			III			IV			V			VI			VII		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
	1	He			Li			Be			B			C			N			O			F		
A	2		Ne			Na			Mg			Al			Si			P			S			Cl	
	3			Ar			K			Ca			Sc			Ti			V			Cr			Mn
	1	Fe			Co			Ni			Cu			—			—			—			Zn		
B	2		—			—			—			Ga			Ge			As			Se			Br	
	3			Kr			Rb			Sr			Y			Zr			Nb			Mo			Ru
	1	Rh			Pb			—			—			Ag			—			—			Cd		
C	2		—			—			—		In				Sn			Sb			Te			J	
	3			Xe			Cs			Ba			La			Ce			Nd			Pr			(Sm)
	1	(Eu)			(Gd$_1$)			(Gd$_2$)			(Gd$_3$)			(Tb$_1$)			(Tb$_2$)			(Dy$_1$)			(Dy$_2$)		
D	2		(Dy$_3$)			(Ho)			(Er)			(Tu$_1$)			(Tu$_2$)			(Tu$_3$)			(Yb)			(Lu)	
	3			—			—			—			—			—			Ta			W			Os
	1	Ir			Pt			Au			Hg			Tl			Bi			Pb			—		
E	2		—			—			—			—			—			—			—			—	
	3			—			—			Ra			—			Th			—			U			—

FIGURE 6.4 Van den Broek table of 1911. From Das Mendelejeffsche ‘kubische” periodische System der Elemente und die Einordnuung der Radioelemente in dieses System, *Physikalishe Zeitschrift*, 12, 490–497, 1911, p. 491. This version is from T. Hirosige, The Van den Broek Hypothesis, *Japanese Studies in the History of Science*, 10, 143-162, 1971. p. 149, (by permission from the publisher).

> If this cubic periodic system should prove to be correct, then the number of possible elements is equal to the number of possible permanent charges of each sign per atom, or to each possible permanent charge (of both signs) per atom belongs a possible element.

Van den Broek was suggesting that since the nuclear charge on an atom was half its atomic weight, and the atomic weights of successive elements increased in stepwise fashion by two, then the nuclear charge defined the position of an element in the periodic table. In other words, each successive element in the periodic table would have a nuclear charge greater by one than the previous element. In making this proposal, van den Broek was going beyond Rutherford and Barkla, neither of whom had been primarily concerned with elements in the periodic table. Whereas Rutherford and Barkla realized that $Z \approx A/2$, van den Broek also realized that $Z \approx A/2$ = atomic number. As the well-known physicist and author Abraham Pais has commented, "Thus based on an incorrect periodic table and on an incorrect relation ($Z \approx$ A/2), did the primacy of Z as an ordering number of the periodic table enter physics for the first time."[15]

But van den Broek's claim to fame does not lie just with this crude premonition of atomic number. By 1913, he abandoned his cubiform table and replaced it with an elaborate two-dimensional version (figure 6.5) and the clearly stated rule that "the serial number of every element in the sequence ordered by increasing

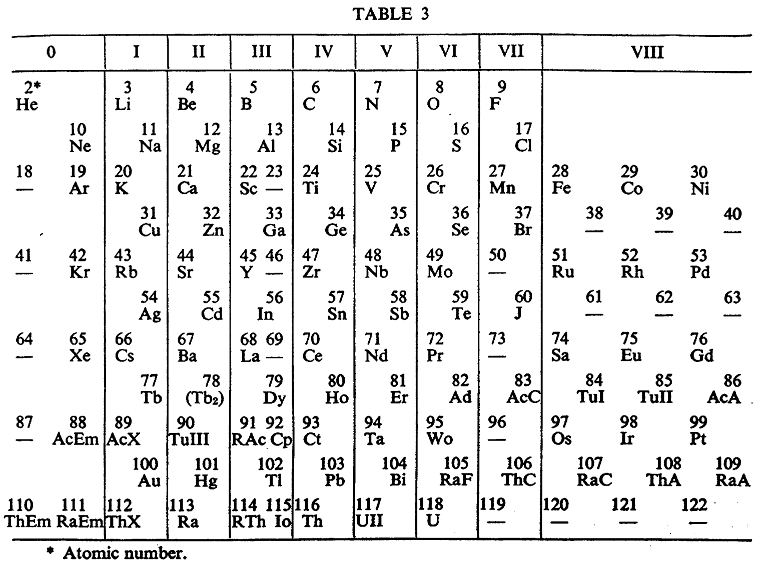


TABLE 3

0		I	II	III	IV	V	VI	VII	VIII		
2* He		3 Li	4 Be	5 B	6 C	7 N	8 O	9 F			
	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl			
18 —	19 Ar	20 K	21 Ca	22 23 Sc —	24 Ti	25 V	26 Cr	27 Mn	28 Fe	29 Co	30 Ni
		31 Cu	32 Zn	33 Ga	34 Ge	35 As	36 Se	37 Br	38 —	39 —	40 —
41 —	42 Kr	43 Rb	44 Sr	45 46 Y —	47 Zr	48 Nb	49 Mo	50 —	51 Ru	52 Rh	53 Pd
		54 Ag	55 Cd	56 In	57 Sn	58 Sb	59 Te	60 J	61 —	62 —	63 —
64 —	65 Xe	66 Cs	67 Ba	68 69 La —	70 Ce	71 Nd	72 Pr	73 —	74 Sa	75 Eu	76 Gd
		77 Tb	78 (Tb$_2$)	79 Dy	80 Ho	81 Er	82 Ad	83 AcC	84 TuI	85 TuII	86 AcA
87 —	88 AcEm	89 AcX	90 TuIII	91 92 RAc Cp	93 Ct	94 Ta	95 Wo	96 —	97 Os	98 Ir	99 Pt
		100 Au	101 Hg	102 Tl	103 Pb	104 Bi	105 RaF	106 ThC	107 RaC	108 ThA	109 RaA
110 ThEm	111 RaEm	112 ThX	113 Ra	114 115 RTh Io	116 Th	117 UII	118 U	119 —	120 —	121 —	122 —

* Atomic number.

FIGURE 6.5 Van den Broek's table of 1913. From Die Radioelemente das Periodische System und die Konstitution der Atome, *Physikalische Zeitschrift*, 14, 32-41, 1913, table on p. 37. This version is from T. Hirosige, The Van den Broek Hypothesis, *Japanese Studies in the History of Science*, 10, 143-162, 1971. p. 152, (by permission from the publisher).

atomic weight equals half the atomic weight and therefore the intra-atomic charge."[16] Although this step takes matters a little further by mentioning serial numbers for each of the elements, it is still somewhat incorrect in being tied rather firmly to atomic weight, albeit atomic weight divided in half. Nevertheless, van den Broek's article was cited by no less a person than Niels Bohr in his trilogy paper of 1913, in which he introduced quantum theory to the atom.[17]

Van den Broek's most significant contribution[18] came in another short communication to *Nature* magazine, published in 1913, in which he explicitly connected the serial number with the charge on each atom and disconnected it from atomic weight: "The hypothesis [about the serial number of the elements being equal to Z] holds good for Mendeleev's table but the nuclear charge is not equal to half the atomic weight."[19] Van den Broek was able to take this important liberating step on the basis of more scattering experiments by Geiger and Marsden, which he analyzed in detail and discussed in his short note. This contribution was praised by Soddy in the next issue of *Nature* and one week later also by Rutherford, who nevertheless privately resented the intrusion of amateurs. It was at this point that Rutherford actually coined the expression "atomic number":

> The original suggestion made by van den Broek that the charge on the nucleus is equal to the atomic number [i.e., the serial number in the periodic table] and not to half the atomic weight seems to me very promising.[20]

Henry Moseley

So it was the amateur scientist van den Broek who confounded all the professional experts and first perceived the importance of atomic number as the ordering criterion for the elements. But as is often the case with scientific discoveries, it is the person who completes the task who is given the most credit, as seen in the case of Mendeleev and the discovery of periodicity.

Such is the case of Henry Moseley (figure 6.6), who died in the First World War at the tender age of 26, before anyone outside the then very small circle of atomic physicists had heard of him. His subsequent fame lies in two brief articles that firmly established that atomic number, rather than atomic weight, was indeed a superior ordering principle for the elements. In addition, he was able to lay the groundwork by which others could settle conclusively that there were a total of 92 naturally occurring elements and could specify precisely where the remaining gaps were situated in the periodic table.

Moseley went to work as a research student with Rutherford, who was at this time in Manchester. There, he was given a project connected with radioactivity.[21] In 1911, Moseley published an article with a fellow graduate student, the Polish born chemist Kasimir Fajans, concerning the measurement of half-lives of some radioactive products obtained from the element actinium.[22]

FIGURE 6.6 Henry Moseley. Photo from author's collection used by permission from Emilio Segrè Collection.

A year later, Max von Laue in Zürich was investigating the nature of X-rays. Believing that they were extremely short electromagnetic rays and therefore should exhibit interference effects, von Laue was attempting to diffract X-rays by bouncing them off planes of atoms in crystalline substances such as sodium chloride.[23] By this time, it was known that X-rays came in two varieties. The first was a type originally observed by Röntgen, which were produced when electrons were stopped by some means, such as the glass walls of an evacuated Crookes tube. Second, Charles Barkla had discovered another kind of X-ray phenomenon brought about when electrons struck targets made of metals. Each different metal would produce X-ray lines showing a characteristic frequency. It was these X-rays, the ones coming off a metal target, and in particular the so-called Kα rays, that Moseley would exploit in his own research.[24]

Moseley made it clear in his articles that he was essentially setting out to test van den Broek's speculation regarding the characterization of each element according to its atomic number. In addition, it is known that he had several meetings with the young Bohr while he, too, was a visitor in Rutherford's Manchester laboratory around 1912–1913. Bohr and Moseley discussed the question of the ordering of nickel and cobalt, an example of pair reversal. Bohr is known to have favored placing cobalt before nickel, to which Moseley is said to have responded "we shall see."[25] Moseley devised an ingenious apparatus in which many different metal plates could be rotated so that each one would become the target for a beam of electrons, and the emitted Kα X-rays would be measured.[26] He first experimented on 14 elements, 9 of which, titanium to zinc, formed a continuous series in the periodic table.[27] Moseley discovered that a plot of the frequency of the lines of the K series of spectral lines of each element was directly proportional to the square of an integer representing the position of each successive element in the periodic table. He found that the frequency, n, of the Kα X-rays obtained from each sample target varied according to an expression of the form

$$n \propto Q^2$$

where Q is a number that increases by a constant amount on moving through the elements.

Moseley had discovered a fundamental quantity that increased by regular intervals as he moved through his sequence of elements in the order in which they appeared in the periodic table. He quickly recognized this quantity as the positive charge on the nucleus, or van den Broek's atomic number. As he stated:

> We have here a proof that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus, of the existence of which we already have definite proof.[28]

Moseley acknowledged the previous work of Barkla, van den Broek, and Bohr, all of whom had anticipated his own findings. He also showed that $Q = N - 1$, where N represents the number of unit charges in the nucleus and therefore the atomic number.

Moseley's second famous paper appeared in print in April 1914. He now reported measurements on a further 30 elements. By examining the K series from aluminum to silver, and the L series of spectral lines from zinc to gold, he found a general expression of the form,

$$n \propto A(N - b)^2,$$

where $b = 1$ for the K series and

$$A \propto (1/1^2 - 1/2^2)$$

Similarly, for the L series $b = 7.4$ and

$$A \propto (1/2^2 - 1/3^2)$$

As soon as Moseley had established the importance of atomic number experimentally, he began to apply this work in settling various questions regarding new elements that had been claimed by various chemists. A total of approximately 70 proposed new elements competed to fill the 16 gaps in Mendeleev's periodic table. Moseley succeeded in showing that many of these were spurious and was able to resolve some priority disputes regarding the discovery of certain elements.

For example, a Japanese chemist, Masataka Ogawa, claimed to have isolated an element that he called nipponium and that he believed to be Mendeleev's eka-manganese.[29] Moseley was able to show that this claim was unfounded since the sample provided by Ogawa did not show the required atomic number when subjected to Moseley's spectral analysis. Similarly, coronium, nebullium, casseopeium, and asterium, which appeared on many early periodic tables, often between hydrogen and lithium, could all be dismissed as spurious elements.[30]

Moseley's work was also used to settle the question of the placement of the rare earth elements, a task that had eluded Mendeleev and other early pioneers of the periodic table. Mendeleev had stated that the placement of the rare earths was one of the most difficult problems of all those confronting the periodic law. The rare earths were notoriously difficult to separate chemically. Since they appeared to differ only slightly in atomic weight and properties, no one had been able to find a satisfactory way of fitting them into the periodic table. According to William Crookes,

> The rare earths perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying, and murmuring strange revelations and possibilities.[31]

Georges Urbain, a French chemist known for his work on the isolation of rare earth elements, traveled to Oxford in order to meet Moseley after hearing of his groundbreaking work. As the story goes, Urbain handed Moseley a sample containing a mixture of rare earths and challenged him to identify which elements were present. After a matter of about one hour, Moseley is said to have surprised Urbain by correctly identifying the presence of erbium, thulium, ytterbium, and lutetium in the Frenchman's sample. The same feat had taken Urbain several months to achieve by chemical means. Urbain then asked Moseley to tell him the relative amounts of the various elements in the sample and was again astonished to receive an answer that coincided almost exactly with his own laborious chemical analysis.

Moseley's work clearly showed that successive elements in the periodic table have an atomic number greater by one unit. From this fact, Moseley and others could identify which gaps remained to be filled in the periodic system and found that there were a total of seven such cases still waiting to be discovered. Unlike previous lists of gaps, this list was now completely definitive and included the precise atomic numbers of the still elusive elements, which were 43, 61, 72, 75, 85, 87, and 91.[32]

The clarification that Moseley brought to the periodic table represents one of the finest examples of the reductive power of physics in the field of chemistry. Most lingering problems regarding pair reversals, such as those concerning tellurium and iodine, which had plagued Mendeleev throughout his career, were thereby resolved. Furthermore, Moseley's work made it easier to deal with the profusion of apparent new "elements" that emerged as a result of research on radioactive phenomena. Two substances could be regarded as being the same element if, and only if, they showed the same value of atomic number, which could be clearly measured by Moseley's method.

Filling the Remaining Gaps

The seven remaining gaps in the periodic table were gradually filled, though not without further controversy in spite of the conclusive nature of Moseley's atomic number method.[33] The first of these was element 91, discovered by Otto Hahn[34] and Lise Meitner in 1917.[35] The element behaved in the manner described by Mendeleev, who had given it the provisional name eka-tantalum. It now became known as protactinium but was not isolated until the year 1934 by Aristide Grosse in Germany.

Element 72, or hafnium, has a rich and controversial story associated with its discovery.[36] Several researchers, including Urbain, independently claimed to have discovered the element but were later found to have been mistaken. In 1923 Dirk Coster and György von Hevesy, working in the Niels Bohr Institute in Copenhagen, finally succeeded in isolating the element, naming it for *Hafnia*, Latin for Copenhagen. According to most accounts, Bohr had first made a theoretical prediction that the element would be a transition metal rather than a rare earth. In fact, some chemists already shared this opinion. As discussed in chapter 8, Charles Bury had also predicted that the element would be a transition metal and had even arrived at its electronic configuration before Bohr.

Element 75, called rhenium, was first discovered in Berlin in 1925 by Walter Noddack, Ida Tacke, and Otto Berg, who isolated it and used Moseley's X-ray method to confirm the presence of the new element. These scientists were also looking for element 43, Mendeleev's eka-manganese, and claimed to have found it in the same ores, calling the new element masurium after Noddack's native region of Prussia. They also published X-ray data for masurium, but it was discredited by others for a variety of reasons. The distinction of discovering element 43 went to Carlo Perrier and Emilio Segrè, who obtained it 12 years later, in 1937, at the University of California–Berkeley. They named the new element technetium to reflect the fact that it had been artificially synthesized as a byproduct in a nuclear reaction.[37]

In 1939, an element subsequently named francium, number 87, was discovered in Paris by Marguerite Perey, and in 1940 Segrè discovered astatine, element 85. The final piece of the jigsaw puzzle, element 61, promethium, was finally obtained as a byproduct in a nuclear reaction. The discoverers on this occasion were Jacob Marinsky, Lawrence Glendenin, and Charles Coryell.[38]

What Moseley Did Not Achieve

As with so many scientific heroes, perhaps more so in this case because of his early death, the claims for what Moseley is supposed to have achieved far outpace the truth. The hagiography of Moseley is constantly propagated by science textbooks, sometimes in a sincere attempt to simplify the account, but it also occurs in more detailed historical treatments. Moseley did not personally settle the question of how many naturally occurring elements exist. Nor did he even definitively resolve the question of how many elements exist between aluminum (13) and gold (79), which marked the boundaries of his own studies. By assuming that aluminum is the 13th element, Moseley argued that there could be only 79 elements up to and including gold (79).

Limiting the elements to 79 left only three remaining gaps in the periodic table, located at atomic numbers 43, 61, and 75. But Moseley could not be confident of this prediction since he did not have pure samples of some of the rare earths. X-ray spectra were not available for terbium (65), dysprosium (66), thulium (69), ytterbium (70), and lutetium (71), and this led him to assert incorrectly the existence of three forms of thulium, named thulium, thulium I, and thulium II. This assignment in turn meant that such elements as ytterbium and lutetium were advanced by one place, so no vacant space was left at element 72. Moseley was unable to place Urbain's keltium, which eventually turned out to be the same as lutetium, discovered by Urbain a few years previously. When matters were resolved, after Moseley's early death, only one form of thulium remained, and ytterbium and lutetium were found to have atomic numbers of 70 and 71, respectively. This meant that there was a vacant gap at 72 for a new element between lutetium and tantalum, the element that would eventually be named hafnium.

Since his experiments did not go beyond gold, or atomic number 79, Moseley certainly did not show that uranium is element 92, as is often claimed. This honor went to the spectroscopist Manne Siegbahn, working in Sweden, in 1916. Finally, even the central achievement invariably associated with Moseley, the realization that atomic number is equal to the number of positive charges in the nucleus, was not conclusively settled until some time later.

In 1920, James Chadwick, who 12 years later would discover the neutron, reanalyzed Moseley's work. He discovered that the choice of value for the constant $b = 7.4$ was not as inevitable as Moseley had claimed. It was still possible in principle for an atomic number not to equal the number of positive charges in the nucleus, and this in turn would have implied that there might be more than 13 elements from hydrogen to aluminum inclusive. Chadwick therefore decided to make some independent measurements of the charges on various nuclei using a refined version of Geiger and Marsden's experiment with alpha rays. Only after this work had been carried out and atomic charges been successfully measured by a second method did Chadwick announce the confirmation of Moseley's simple idea. Atomic number does indeed equal the number of positive charges in the nucleus of any atom.[39]

Philosophical Debates Reopened

Van den Broek's suggestion, and Moseley's experimental work on atomic number, had the effect of rehabilitating Prout's hypothesis, which had proposed that all elements were composites of hydrogen. The atomic numbers of all the elements were indeed exact multiples of the atomic number for hydrogen, which is 1. More generally, the work of van den Broek and Moseley revitalized some philosophical notions of the unity of all matter that had been so harshly criticized by Mendeleev, among others. By now, Thomson had shown that the electron was common to all elements and Rutherford had established that electric particles were present in the nuclei of all elements. Moseley had added the fact that all nuclei seemed to consist of an integral number of positive charges. There clearly seemed to be some form of underlying unity behind the apparent diversity of the elements. This view was strengthened further when Rutherford discovered that elements could be transmuted into each other through the use of radioactive techniques, thus once again recalling the ancient alchemical notion of the fundamental unity of all matter.

Nevertheless, the cause of the initial rejection of Prout's hypothesis, in its original form, had not been resolved. As described in chapter 2, this was the fact that certain elements such as chlorine (35.46) and lead (207.20) had nonintegral atomic weights. This particular puzzle had to await the discovery of isotopy, which is generally attributed to the chemist Frederick Soddy.

Isotopy

The idea that any element can consist of different kinds of atoms can be traced to a remark made by William Crookes in 1886:[40]

> I conceive that when we say the atomic weight of calcium is 40, we really explain the fact, while the *majority* of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on.[41]

The first clear elaboration of isotopy, however, came much later and belongs to the English chemist Soddy, who began as one of Rutherford's collaborators, like so many others who made important contributions to atomic science. After research in chemistry at Oxford, Soddy joined Rutherford at McGill University in Montreal in 1900 and participated in much of the work that established the concept of radioactive half-lives and the reality of radioactive transmutation.

During this time, other scientists were also exploring radioactivity and in the process were discovering new elements. The first of these were polonium, radium, actinium, and radon, followed by another 30 or so suspected new elements, most of which would turn out to be isotopes of existing elements.[42] Some, like van den Broek, tried desperately to incorporate all these new species into the periodic table. Others, including the Swedes Daniel Strömholm and Theodor Svedberg, realized that there were great similarities among many of these new species. As Jan van Spronsen notes, in his book on the periodic table, Strömholm and Svedberg can also be regarded as having anticipated the existence of isotopes. For example, they grouped together radium emanation, actinium emanation, and thorium emanation into one single place in their periodic system (table 6.1). Similarly, radium, actinium X, and thorium X were all made to occupy a single place.[43] Without explicitly stating the concept and drawing out its full consequences, Strömholm and Svedberg had realized that several species can occupy a single space in the periodic table, a concept Soddy was soon to name isotopy from the Greek *iso* (same) and *topos* (place).

Another strand of development came from several attempts to separate some of these new radio-elements chemically, which ended in failure. First of all, in 1907 Herbert McCoy and William Ross concluded that, in the case of thorium and radiothorium, "Our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes,"[44] a comment Soddy considered the first definitive statement of the chemical inseparability of what were soon to be called isotopes. Soddy himself wrote in the same year that there seemed to be no known method of separating thorium X from mesothorium. They were in fact two isotopes of thorium. Similar cases began to multiply. Bertram Boltwood discovered the radio-element ionium, which could not be chemically separated from thorium. In another famous case, Rutherford asked Györgi von Hevesy and Fritz Paneth to try to separate radio-lead from ordinary lead and likewise failed to do so, in spite of using 20 different chemical methods. Their work was not entirely in vain, however, since it led to the development of the use of radioactive tracers, which have become an indispensable tool in modern chemistry and biochemistry.

In 1911, Soddy wrote the following comments regarding the various series of very similar radioactive elements that had recently been discovered:

> The conclusion is scarcely to be resisted that we have in these examples no mere chemical analogues but chemical identities.... Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several different atomic weights, or that any atomic weight is not merely a mean number. The constancy of atomic weight, whatever the source of the material, is not a complete proof of homogeneity.[45]

Table 6.1

Strömholm and Svedberg's fragment table.

	0 Row	*1 Row*	*2 Row*	*3–4 Row*
5 period	Xe	Cs	Ba	La – Yb
	Ra – Em	—	Ra	Ionium – (UX-Rad.U)
	Akt – Em	—	Akt X	Rad.Akt.– Akt.
6 period	Th – Em	—	Th X	Rad.Th – Mes.Th-Th

D. Stromholf, T. Svedberg, Untersuchungen über die Chemie der radioaktiven Grundstoffe. II. Die Aktiniumreihe *Zeitschrift für anorganische Chemie*, 63, 197-206, 1909, table on p. 204. The abbreviation Rad stands for radio, a prefix used to denote suspected new elements, such as radio-thorium, most of which turned out to be isotopes. Em denotes the term emanation meaning substances emanating from a particular element. Akt was the German abbreviation for the modern symbol Ac for actinium.

The first time Soddy actually used the term "isotope"[46] was in an article in 1913, where he wrote,

> The same algebraic sum of positive and negative charges in the nucleus, when the arithmetic sum is different, gives what I call "isotopes" or isotopic elements, because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also.[47]

The first sentence in this quotation might appear to be a mistake, and in a sense it is since there are no negative charges in the nucleus. What Soddy was referring to was beta particles, which are identical to electrons but are created in the nucleus. In modern terms, beta decay involves the transformation of a neutron into a proton, accompanied by the emission of a beta particle. Interestingly, the notion that beta particles originate in the nucleus was first proposed by van den Broek and later supported by several others, including Soddy.

Many aspects of the problem of inseparable elements were clarified when Soddy and Fajans independently suggested what became known as the group displacement laws. They stated that the emission of an alpha particle from the atom of an element produces an element located two places to the left, while the emission of a beta particle resulted in a movement of one position to the right in the periodic table. It followed that the elements between lead and uranium in the periodic table could exist as more than one kind of atom, differing in mass but displaying the same chemical behavior. For example, if an atom of uranium-235 ($Z = 92$) undergoes alpha decay, it forms an atom of thorium-231 ($Z = 90$). Meanwhile, an atom of actinium-230 ($Z = 89$) can undergo beta decay to form an atom of thorium-230 ($Z = 90$). The products of both radioactive decays are atoms of the same element but have different atomic weights.[48] Fajans coined the term "pleiad" to mean a group of chemically identical atoms with different atomic masses, but his term was not generally adopted.[49]

Only now did it become clear why such elements as tellurium and iodine, and other pair reversals, had caused so much trouble for the pioneers of the periodic system. Tellurium has a lower atomic number than iodine and so should genuinely be placed before iodine, as Mendeleev and others had guessed. In addition, it was now clear that the higher atomic weight of tellurium was due to a higher average mass of the various isotopes that made up a terrestrial sample of this element.

The final piece of evidence that completed this episode regarding isotopes and the periodic table was provided by the Harvard chemist Theodore W. Richards in 1914. Although the idea that isotopes of the same element, arising from different mineral sources, might have different atomic weights had been discussed for a few years, it had not been directly examined. Richards, an acknowledged expert on atomic weight determination, was ideally placed to undertake this research. Since the element lead had been found to be the end point in several radioactive decay series, it was reasonable to expect this element to show some variation in weight.

Any such variation would depend on the mineral source used, since any lead found in earth might have resulted from one of several different elements by a process of natural transmutation brought about by radioactive decay.

Fajans's and Soddy's independent work on the displacement series had shown that the stable end products of all three radioactive decay series, as well as common lead, were chemically indistinguishable or, in the new terminology, were all isotopes of lead. What Richards set out to discover was whether different naturally occurring mixtures of these isotopes might show different atomic weights, as one might expect. In the report by Richards and a young German student, Max Lembert, they called their results "amazing." They had found atomic weights of lead differing from that of common lead by as much as 0.75 of an atomic weight unit, an amount that was several times larger than the error associated with their experimental method. Repeated purification of lead samples from various radioactive origins produced no changes in their atomic weights. Encouraged by this research, others tried to find other ores of lead in the hope of showing an even greater variation in atomic weights. These efforts eventually produced a lowest value of 207.05 and a highest value of 207.90.

Postscript on Triads

The discoveries discussed in this chapter effectively revived Prout's hypothesis as well as the related notion of the unity of matter, two philosophical ideas discussed in chapter 2. The other main theoretical notion discussed in chapter 2, that of triads, also received a form of rehabilitation. The discovery of triads had given the very first hint that groups of three elements were related to each other. These relationships were not just in chemical similarities but were also numerical, in that the atomic weight of one of the three elements in a triad was shown to be approximately the arithmetic mean of the weights of the other two.

This idea had been at the root of Döbereiner's work, which is often taken as marking the birth of the modern periodic system. However, there were limits to the applicability of the triad concept, and it is probably fair to say that much time was wasted by other researchers in trying to uncover triads where they simply did not exist. Some pioneers, including Mendeleev, made it a point to turn their backs on the two original concepts of Prout's hypothesis and the existence of numerical triads. This attitude certainly seems to have paid dividends for Mendeleev in that he made progress where others had failed to do so.

The problem with triads and, indeed, Prout's hypothesis is easy to discern in retrospect. It is simply that atomic weight, which both concepts draw upon, is not the most fundamental quantity that can be used to systematize the elements. Atomic weight such as that of lead, as just discussed, depends on the particular geological origin of the sample examined. In addition, the measured weight is an average of several isotopes of the particular element. Atomic number, on the other hand, is fundamental and correctly characterizes, as far as presently known, the distinction between one element and the next. Prout's hypothesis is brought back to life if one considers that all the elements are composites of the atomic number, or charge, of the element hydrogen, which has a value of 1.

In the case of triads, the adoption of atomic number has an intriguing consequence that has seldom been discussed. It is that about 50% of all vertical triads based on atomic number, rather than atomic weight, are absolutely exact![50] This remarkable result is quite easy to appreciate by referring to the long form of the modern periodic table (figure 6.7).

By considering elements from rows 1, 2, and 3, such as helium, neon, and argon, a perfect atomic number triad is obtained:

He	2
Ne	$10 = (2 + 18)/2$
Ar	18

Or, from rows 3, 4, and 5:

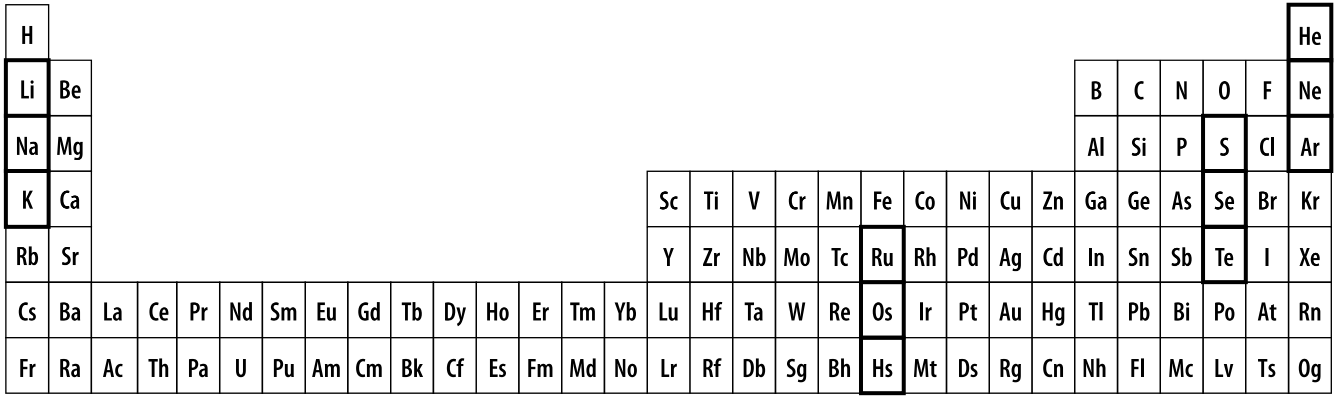
P	15
As	$33 = (15 + 51)/2$
Sb	51

Or, from rows 5, 6, and 7:

Y	39
Lu	$71 = (39 + 103)/2$
Lr	103

Alternatively, any triads taken from combinations of elements in rows 2, 3, 4 or from rows 4, 5, 6, and so on, do not give perfect triads.

This works perfectly, albeit in only 50% of possible triads, because the length of each period repeats just once in the long-form periodic table, with the exception of the very first short period. The full sequence is 2, 8, 8, 18, 18, 32, 32, and so on. So, if one selects any element, then there is a 50% chance that the element above and below the selected element, in the same column of the periodic table, will have atomic numbers lying at an equal distance away from the original element. If this is the case, then it follows trivially that the second element in the sequence will lie exactly midway between the first and third elements. In numerical terms, its atomic number will be the exact mean of the first and third elements, or in other words, the atomic number triad will hold perfectly. All one needs to do is to pick a middle element from the first of a repeating pair of periods. Thus, half of all the elements are good candidates. This phenomenon falls out mathematically from the fact that all periods repeat (except for the first one) and that the elements are characterized by whole number integers. It would appear that the original discoverers had



H																														He
Li	Be																								B	C	N	O	F	Ne
Na	Mg																								Al	Si	P	S	Cl	Ar
K	Ca														Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr														Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

FIGURE 6.7 Slightly modified long-form table showing that about 50% of all atomic number triads are exact. The heavily outlined elements represent examples of perfect atomic number triads.

accidentally stumbled upon the fact that some periods of elements repeat twice. What held them back was that these repeat distances vary in length and, of course, the fact that they were operating with the vagaries of atomic weight data.

It is somewhat amusing to think that the ancient notions of Prout's hypothesis and triads of elements, which were initially so productive and later so strongly criticized, have been shown to be essentially correct, and that the reason for their being essentially correct is now fully understood. In fact, the philosopher of science Imre Lakatos used the example of Prout's hypothesis to illustrate a theory making a "comeback" after being apparently refuted.[51]

Postscript on Atomic Mass

We cannot leave the important subject of atomic mass without discussing the way that this quantity is defined in modern chemistry.[52] As we have seen in previous chapters, the original standard with which the masses of all other atoms were compared was that of hydrogen. This is an obvious choice given that hydrogen has the lightest atom and thus avoids the inconvenience of obtaining any values less than unity for other atoms. The modern standard, however, is carbon, and more precisely one single isotope of this element, namely, ^{12}C, whose atom is assigned a mass of exactly 12.00 atomic mass units. Consequently, one atomic mass unit is equivalent to one-twelfth of the mass of a ^{12}C isotope. The benefit of choosing this isotope as having a mass of 12 rather than 1 is that the older values have not needed to undergo any drastic changes.

The fundamental reason for selecting the modern standard as an atom of an element other than hydrogen represents an interesting and not so well-known aspect of atomic physics. All atoms with the exception of the most abundant isotope of hydrogen or protium, ^{1}H, have more than one particle in their nuclei. Protium is therefore the only isotope with a zero binding energy, a concept that is discussed in greater detail in chapter 10. The main point is that the standard atom against which all others are compared should have a non-zero binding energy and preferably a value that is typical of most atoms in the periodic table.

Consider the following imaginary story that aims to explain the issue. We wish to artificially construct an isotope of an element containing 50 protons and 70 neutrons by individually selecting such particles and adding them to our imaginary nucleus in order to allow them to combine and reach stability. Since binding energy represents about 0.8% of the mass of a typical atom, our so constructed 120 nucleon nucleus will have a mass of approximately 119 nucleons when weighed.[53] This would mean that an isotope with a mass number of 120 would have a mass of 119, a feature that would no doubt introduce some confusion.[54] In order for the mass of the atom in question to correspond more closely to the mass number of an isotope, the binding energy must be taken into account from the outset. The simplest way to achieve this goal is to select an atom that has a reasonably typical binding energy, rather than work with hydrogen whose most abundant isotope contains just a proton and therefore zero binding energy. In principle, any element whose binding energy falls in the typical zone between 6 and 9 eV could have been selected. There is nothing special about carbon, except that it also forms more compounds than any other element, and as a consequence any possible further errors can be minimized.[55]

Conclusion

This chapter examines the various lines of research on the nucleus of the atom that contributed to the evolution of the periodic system. This represents the first time that work in physics began to have a profound impact on the way the periodic system was understood. Perhaps the most important of these contributions has been the concept of atomic number, first argued for by van den Broek and first experimentally demonstrated by Moseley. The importance of this work is that, for the first time, chemists now had an unambiguous method for determining exactly how many elements were present and where in the periodic system any gaps might still remain to be occupied by new elements.

Notes

1. An interesting semi-popular book on the life and work of Boltzmann is D. Lindley, *Boltzmann's Atom*, Free Press, New York, 2001.

2. Whether or not, or to what extent, Thomson discovered the electron has been the focus of much historical research. See various articles in J. Buchwald, A. Warwick (eds.), *Histories of the Electron: The Birth of Microphysics*, MIT Press, Cambridge, MA, 2001.

3. This is not exactly the case. Isotopes of hydrogen, e.g., give rise to compounds that do show chemical differences. Nevertheless, for most purposes, chemical differences between the isotopes of an element may be taken to be insignificant.

4. It is by no means clear that Becquerel was the first to discover radioactivity, contrary to most accounts and, indeed, the one given here. See T. Rothman, *Everything's Relative*, Wiley, Hoboken, NJ, 2003, pp. 46–52. Rothman makes a very good case for the prior discovery by Abel Niepce de Saint-Victor, who was the brother of Joseph-Nicéphore Niepce, who made the first ever photographic image.

5. The story of her early education, which has been told many times, is truly heroic, especially given the difficulties experienced by women wishing to study in universities at the turn of the nineteenth century. Curie was forced to go to Paris because Polish universities simply did not admit women at that time. After working for about six years as a governess and teacher, she had saved enough money to undertake a trip to Paris to enroll at the Sorbonne in 1891. While living under very meager conditions, she began by attending physics lectures and succeeded in graduating first in her class only two years later. She was immediately taken on to do some research on the magnetic properties of steels in the nearby laboratory of Pierre Curie, who was already a prominent French physicist. Eventually, they would marry. During

this period, she also undertook another undergraduate degree in mathematics, finishing second in her class. She registered for a doctoral degree, which would be the first such degree awarded to a woman anywhere in Europe. The research she did for this degree would win her the first of her two Nobel Prizes. There are a number of detailed historical studies of Madame Curie, including S. Quinn, *Marie Curie, A Life*, Simon & Schuster, New York, 1995.

6. B. Bensaude, I. Stengers, *A History of Chemistry*, Harvard University Press, Cambridge, MA, 1996, quoted from p. 227.

7. In any case, the same authors are surely mistaken when they wrote, "In each place in Mendeleev's table there was no longer just an element, but a certain number of distinct atoms, all having the same chemical properties, but distinguished by their atomic weights and the instability of their nuclei …." B. Bensaude, I. Stengers, *A History of Chemistry,* Harvard University Press, Cambridge, MA, 1996, p. 230.

8. J. Perrin, Le Mouvement Brownien de Rotation, *Comptes Rendus*, 149, 549–551, 1909; H. Nagaoka, Motion of Particles in an Ideal Atom Illustrating the Line and Band Spectra and the Phenomena of Radioactivity, *Bulletin of the Mathematical and Physical Society of Tokyo*, 2, 140–141, 1904.

9. C.G. Barkla, Note on the Energy of Scattered X-radiation, *Philosophical Magazine*, 21, 648–652, 1911. This relationship held true for elements with atomic weights equal to or less than 32 ($A \leq 32$). In terms of atomic number, this is equivalent to the first 16 elements, or hydrogen to sulfur. It should also be noted that by this time it was understood that X-rays were produced by electrons.

10. A.J. van den Broek, The α Particle and the Periodic System of the Elements, *Annalen der Physik*, 23, 199–203, 1907.

11. In fact, the α particle is a helium atom that has been stripped of both of its orbiting electrons. It has a mass of 4 and a charge of +2.

12. A.J. van den Broek, Das Mendelejeffsche 'kubische" per iodische System der Elemente und die Einordnuung der Radioelemente in dieses System, *Physikalische Zeitschrift*, 12, 490–497, 1911.

13. A.J. van den Broek, The Number of Possible Elements and Mendeléeff's "Cubic" Periodic System, *Nature*, 87, 78, 1911.

14. Van den Broek did not make this connection explicit, with the result that most writers on the periodic table and in history of science generally have failed to notice it. They merely state that van den Broek drew on the work of Rutherford and Barkla and went on to hint at the concept of atomic number. The point is that he had prior grounds for latching onto the work of Rutherford and Barkla. For a detailed account of the work of van den Broek, see E. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016, pp. 41–62.

15. A. Pais, *Inward Bound*, Oxford University Press, New York, 1986, p. 227.

16. A. van den Broek, Die Radioelemente, das periodische System und die Konstitution der Atome. *Physikalische Zeitschrift*, 14, 32–41, 1913.

17. N. Bohr, On the Constitution of Atoms and Molecules, *Philosophical Magazine*, 26, 1–25, 476–502, 857–875, 1913 (known as the trilogy paper). Van den Broek is cited on p. 14.

18. See E. Scerri, *A Tale of Seven Scientists and A New Philosophy of Science*, Oxford University Press, New York, 2016, pp. 41–62. An entire chapter of this book concerns the work of van den Broek. Also see E.R. Scerri, Antonius van den Broek, Moseley and the concept of atomic number. *In For Science, King and Country – Henry Moseley*, eds. R. Edgell, R. MacLeod, E. Bruton, 2018, 102–118.

19. A.J. van den Broek, Intra-atomic Charge, *Nature*, 92, 372–373, 1913.

20. E. Rutherford, The Structure of the Atom, *Nature*, 92, 423, 1913.

21. Moseley's ancestors had all been prominent scientists. His father was a professor of comparative anatomy at Oxford. His grandfather, also called Henry, had been a famous

mathematician and physicist at King's College, London. Henry Moseley the younger followed a rather typical aristocratic academic career in attending the public school Eton and going on to undergraduate studies at Trinity College Oxford.

Moseley's appetite for hard work is shown by the following anecdote: Charles Darwin the younger, the grandson of Charles Darwin of evolution fame and a good friend of Moseley's in Manchester, was later quoted as saying that one of Moseley's many talents was the knowledge of where one could find a meal at three o'clock in the morning in the streets of Manchester.

22. Fajans was visiting Rutherford's lab from Heidelberg at the time.

23. Strictly speaking, the planes in substances such as sodium chloride consist of ions and not atoms.

24. Barkla had actually distinguished two types of characteristic emissions, one more penetrating than the other. These he called K and L series, respectively.

25. As discussed in chapter 7, Bohr was to take the physical explanation of the periodic system to new levels when he began to use quantum theory to write electronic configurations for atoms and to relate these to the periodic table.

26. Moseley conducted the final stages of these experiments in Oxford in the laboratory of his former undergraduate professor John Sealy Townsend, who was able to provide him with space.

27. Three elements were missing between the first and last in the sequence that Moseley examined: phosphorus, sulfur, and scandium.

28. H.G.J. Moseley, Atomic Models and X-Ray Spectra, *Nature*, 92, 554, 1913.

29. Eka-manganese was eventually discovered and named technetium.

30. For further accounts of the discovery of elements and those that turned out to be spurious, see V. Karpenko, The Discovery of Supposed New Elements, *Ambix*, 27, 77–102, 1980; and E. Rancke-Madsen, The Discovery of an Element, *Centaurus*, 19, 299–313, 1976.

31. As cited in B. Jaffe, *Crucibles: The Story of Chemistry from Ancient Alchemy to Nuclear Fission*, Simon & Schuster, New York, 1948.

32. As emphasized further below, Moseley himself did not conclude that seven gaps remained. In fact, his first estimate, based on the available evidence, was that there were just three.

33. A detailed account of the discovery of these seven elements is provided in E. Scerri, *A Tale of Seven Elements*, Oxford University Press, New York, 2013.

34. Hahn would go on to discover the enormously important process of nuclear fission, along with colleagues Hans Strassman and Lise Meitner, thus paving the way to the development of atomic weapons and the later peaceful use of radioactivity in the generation of nuclear power.

35. According to M.E. Weeks and H.M. Leicester, *Discovery of the Elements* (7th ed., Journal of Chemical Education, Easton, PA, 1968), perhaps the most authoritative book on the discovery of the elements.

36. E.R. Scerri, Prediction of the Nature of Hafnium from Chemistry, Bohr's Theory and Quantum Theory, *Annals of Science*, 51, 137–150, 1994.

37. In the first edition of this book, I reported that the claims of van Assche supported those of the Noddacks to the effect that they had isolated element 43. I have now learned that those claims have been refuted. F. Habashi, The History of Element 43–technetium, *Journal of Chemical Education*, 83, 213–213, 2006. For a comprehensive and highly accessible article on many aspects of technetium, including why it is so unstable despite its having a relatively low atomic number, see E.V. Johnstone, M.A. Yates, F. Poineau, A. Sattelberger, K.R. Czerwinski, Technetium: The First Radioelement on the Periodic Table, *Journal of Chemical Education*, 94, 320–326, 2017.

38. Several earlier claims for the detection of naturally occurring element 61 were eventually refuted. Among the names in the course of the early claims were illinium (after Illinois), florentium (after Florence, Italy), and cyclonium (after the use of the cyclotron accelerator). Even the last claim was incorrect, although the eventual discovery was indeed made in a particle accelerator experiment. E.R. Scerri, *A Tale of Seven Elements*, Oxford University Press, New York, 2013; M. Fontani, M. Costa, M.V. Orna, *The Lost Elements: The Periodic Table's Shadow Side*, Oxford University Press, New York, 2014.

39. For a recent edited collection of articles about all aspects of Moseley's life and scientific work, see R.MacLeod, R. Egdell, E. Bruton, *For Science, King & Country: The Life and Legacy of Henry Moseley*, Uniform Press, London, 2018.

40. I should point out that this claim was strenuously disputed by Robert DeKosky in his review of the first edition of this book. R. DeKosky, Book Review of The Periodic Table, Its Story and Its Significance, *Annals of Science*, 65, 461–464, 2008.

41. W. Crookes, Address to the Chemical Section of the British Association, *Chemical News*, 56, 115–126, 1886.

42. A complete list of these radio-elements, including their eventual classification as isotopes of existing elements, can be found in the appendices of A.J. Ihde, *The Development of Modern Chemistry*, Dover Publications, New York, 1984.

43. The symbol X was used in the mathematical sense of "unknown" since it was not known whether in fact these were new elements.

44. H.N. McCoy, W.H. Ross, The Specific Radioactivity of Thorium and the Variation of the Activity with Chemical Treatment, *Journal of the American Chemical Society*, 29, 1709–1718, 1907, Quoted from p. 1711.

45. F. Soddy, *Annual Reports to the London Chemical Society,* 285*,* 1910.

46. According to Fleck, a former student of Soddy's, the term "isotope" was suggested to Soddy by a family friend, Margaret Todd.

47. F. Soddy, Intra-atomic Charge, *Nature*, 92, 399–400, 1913.

48. This explanation is somewhat ahistorical in the use of mass numbers to characterize particular isotopes, e.g., uranium-235 or thorium-231.

49. To anticipate our current knowledge, chemical properties are governed by the number of electrons in an atom and not by its atomic weight. Two or more isotopes of the same element can therefore differ in mass, while having the same atomic number (number of protons) as well as the same number of electrons. The different weights that two or more isotopes of the same element display are due to their having different numbers of neutrons while sharing exactly the same number of protons. In approximate terms, the weight of an atom is given by the sum of the protons, neutrons, and electrons. The neutron was not actually discovered until 1930.

50. Placing hydrogen among the halogens is not so unlikely given that hydrogen can form a singly charged negative ion, as do the halogen elements and the fact that hydrogen forms diatomic gaseous molecules as do fluorine and chlorine. Some periodic tables position hydrogen among the halogens, although not always for the same reason.

51. I. Lakatos, *The Methodology of Scientific Research Programmes*, edited by J. Worrall, G. Currie, Cambridge University Press, Cambridge, 1978. The pages dealing with Prout's hypothesis are 43, 53–555, 118–119, and 223.

52. Another issue concerning atomic weights, or more correctly atomic masses, that has emerged in recent years has been the practice of expressing ranges in the relative atomic weights of elements, rather than one specific value for each element. This has occurred because it is increasingly being recognized that elemental samples from different parts of the world can have varying isotopic compositions. T.R. Coplen, F. Myers, N.E. Holden, Clarifying Atomic Weights: A 2016 Four-Figure Table of Standard and Conventional Atomic

Weights, *Journal of Chemical Education*, 94, 311–319, 2017. Additional articles on aspects of atomic weight can be found in E. Roth, Atomic Weights: Problems Past and Present, *Interdisciplinary Science Reviews*, 2, 1, 75–85, 1977, J. Meja, An Ode to the Atomic Weights, *Nature Chemistry*, 6, 749–750, 2014.

53. Neutrons and protons weigh virtually the same amount, namely, 1.67493×10^{-27} kg (neutron) and $1.67262 \text{ x } 10^{-27}$ kg (proton).

54. Chemists frequently use the terms "atomic weight" and "atomic mass" synonymously. Although this is technically incorrect, it is frequently tolerated in chemistry. I have tried to avoid this practice, especially in this final section that features a comparison of mass numbers with the actual masses of isotopes.

55. I am very grateful to Lee Sobotka, who reviewed the first edition of this book, for enlightening me as to the importance of binding energy in the context of atomic weights. At the same time, I have an uneasy feeling that my last sentence concerning the further reason for selecting carbon may be in error, and I can only hope for readers and reviewers who might be equally helpful in clearing up my own lingering confusion. Sobotka's book review appears in L. Sobotka, *Physics in Perspective*, 10, 374–375, 2008.

CHAPTER

7

The Electron and Chemical Periodicity

J.J. Thomson's discovery of the electron is one of the most celebrated events in the history of physics.[1] What is not so well known is that Thomson had a deep interest in chemistry, which, among other things, motivated him to put forward the first explanation for the periodic table of elements in terms of electrons.[2] Today, it is still generally believed that the electron holds the key to explaining the existence of the periodic table and the form it takes. This explanation has undergone a number of subtle changes. The extent to which the modern explanation is purely deductive or whether it is semiempirical is examined in this chapter.

While Dmitri Mendeleev had remained strongly opposed to any attempts to reduce, or explain, the periodic table in terms of atomic structure, Julius Lothar Meyer was not so averse to reduction of the periodic system. The latter strongly believed in the existence of primary matter and also supported William Prout's hypothesis. Lothar Meyer did not hesitate to draw curves through the numerical properties of atoms, whereas Mendeleev believed this to be a mistake, since it conflicted with his own belief in the individuality of the elements.

This is how matters stood before the discovery of the electron, three years prior to the turn of the twentieth century. The atom's existence was still very much a matter of dispute, and its substructure had not yet been discovered. There appeared to be no way of explaining the periodic system theoretically.[3]

The Discovery of the Electron and Early Models of the Atom

Johnston Stoney first proposed the existence and name for the electron in 1891, although he did not believe that it existed as a free particle. Several researchers discovered the physical electron, including Emil Wiechert in Königsberg, who was the first to publish his findings. Because these early researchers did not seriously follow up on their results, it was left to the British physicist Thomson to capitalize upon and establish the initial observations. These false starts show an interesting parallel with the discovery of the periodic system, where the essential idea of periodicity occurred to a number of scientists, including Émile De Chancourtois, John Newlands, and William Odling, none of whom was able to make much headway in establishing his insights.

While Wilhelm Röntgen discovered X-rays by experimenting with cathode rays, Thomson was one of several physicists who set out to explain the very nature of these cathode rays. The experiments he and others were carrying out typically involved the passage of an electric discharge of about 1000 V through a gas held in a glass tube of about 300 cm in length and 3 cm wide at a pressure of about 0.01 mm of mercury. In 1869, the year of Mendeleev's famous periodic table, Johann Hittorf in Germany had observed that glowing rays were emitted from the cathode, or negative pole, of such an experimental apparatus. Some early workers, such as William Crookes, supported the notion that these "cathode rays" were particles projected from the negative pole and were themselves negatively charged. A number of others working in Germany, such as Heinrich Herz, came to believe that the cathode rays were a form of radiation. In 1897, Wiechert interpreted his own experiments by concluding, "We are not dealing with atoms known from chemistry, because the mass of the moving particles turned out to be 2000–4000 times smaller than the one of the hydrogen atom, the lightest of the known chemical atoms."[4] In the same year, Walter Kaufmann measured the charge-to-mass ratio of cathode rays and found it to be the same in every gas. This fact puzzled him but did not lead him to draw the conclusion that the particle might be a universal constituent of all substances.

It was in this context that Thomson conducted his own research, which, according to the traditional account, led to the discovery of the electron and the realization that it was indeed a constituent of all matter. By now, it was known that cathode rays were negatively charged, and they appeared to be particulate. But there was yet no confirmation of their particle nature. This confirmation would be forthcoming only if it could be shown that cathode rays could be deflected by an electric field, something that had eluded all previous attempts. Thomson succeeded where others had failed by using an extremely high electric charge as well as by ensuring that the glass tube was under vacuum conditions. Under these conditions, the cathode rays finally showed a deflection due to an electric field in 1897.

Moreover, Thomson was able to measure the charge-to-mass ratio of cathode rays and found a value of 770 for such particles emanating from hydrogen atoms. This finding suggested three possibilities: the particles making up the cathode rays bore a very large charge; they had a very small mass; or possibly a combination of the two effects was responsible. It was later found that cathode rays, or electrons, as they became known, had the same charge as hydrogen ions, although of opposite sign, but they had a much smaller mass.[5] Last but not least, Thomson went beyond

Wiechert in that he repeated his experiments with cathode rays produced from various different elements, concluding that the same particle was produced in each case, and that this particle was therefore a fundamental constituent of all matter. Thomson seems to have disliked Stoney's name for the particle, although it had been popularly adopted. He insisted on calling it the "corpuscle," only later capitulating to the popular usage of "electron."

Models of the Atom

The newly discovered electron began to feature in several postulated models of the atom. The French physicist Jean Perrin, like Thomson in England, had conducted experiments on cathode rays. In fact, Perrin had been the first to obtain direct proof that the electron was negatively charged. This was carried out in experiments in which a metal cylinder was placed inside a vacuum tube in order to collect the charge. By drawing on this finding, in addition to the experimental evidence gathered by Thomson, Perrin suggested the first planetary conception of the atom in 1901. He proposed that each atom consisted of one or more highly charged positive bodies, much like a positive sun around which small negative planets, or electrons, were in orbit. Perrin also believed that the total negative charge in the atom would be exactly equal to the total positive charge, in apparent anticipation of current views on the structure of the atom. He stated his hypothesis thus:

> Each atom will consist of one or more highly charged positive bodies, a kind of positive sun whose charge is much higher than that of a corpuscle (electron), and also of a kind of small negative planets, all these bodies gravitating under the action of electrical forces, and with total negative charge exactly equal to the total positive charge, so that the atom is electrically neutral.[6]

A further proposal by Perrin in the same paper seems to foreshadow later work on the connection between the structure of the atom and spectral frequencies: "The gravitational periods of the different masses in the atom might correspond to the different wavelengths of light revealed in the rays of the emission spectrum."[7] In modern terms, the wavelengths of light revealed in the atomic spectra are not related to gravitational periods but to transitions between energy levels, which are characteristic of the various orbitals that the electrons can occupy.[8] In 1903, Hantaro Nagaoka in Japan independently proposed a Saturnian atom in which electrons move in one or more rings around a central body.[9] A translation of one of his lectures was published in 1904 in the *Philosophical Magazine*[10] and was subsequently quoted by leading physicists such as Ernest Rutherford and Henri Poincaré.

In that same year, Thomson began to think specifically about how the electrons might be arranged in the atom. He concluded that the solar system-like atoms of Perrin and Nagaoka would be unstable because the orbiting electrons would continuously radiate energy, eventually falling into the center of the atom. He suggested an alternative model in which the electrons were embedded in the nucleus, circulating within its positive charge. This became known as the "plum pudding" model of the atom. In a paper of 1904, Thomson also published the first set of electronic arrangements, or what today would be called electronic configurations.[11] In taking this step, Thomson went beyond Perrin and Nagaoka in conceiving of the electrons not just as moving around the atom but doing so in a structured manner.

Thomson based his configurations of electrons on the work of an American physicist Alfred Mayer, who had experimented with magnets that were attached to corks and floated in a circular basin of water above which was placed a current-bearing metal coil (figure 7.1). Mayer had found that when up to five magnets were floated, they would form a single ring, but that on the addition of a sixth magnet a new ring would be formed.[12] As more magnets were added, the phenomenon repeated: When a certain number of magnets was reached, the addition of a new magnet caused the formation of yet another ring, thus producing an arrangement of concentric rings. Thomson believed that the same kind of principle might operate in the case of electrons circulating in the atom and began to develop these views in an attempt to explain the periodic table in terms of the electron.

In many respects, Thomson can therefore be regarded as the originator of electronic configurations and of attempts to explain the periodic table in terms of them. Table 7.1 is an extract from one of Thomson's later articles showing how his electron rings were arranged. As with Mayer's cork rings, the presence of five electrons

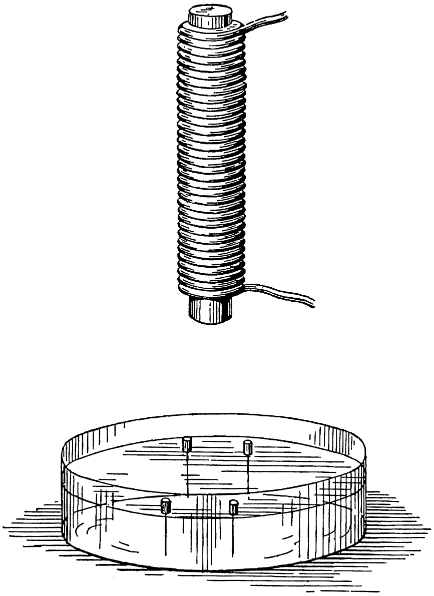


FIGURE 7.1 Mayer's floating magnets from, On the Morphological Laws of the Configurations formed by Magnets floatoing vertically and subjected to the attraction of a superposed magnet; with notes on some of the phenomena in molecular structure which these experiments may serve to explain, Alfred M. Mayer, *American Journal of Science*, 15, 276–277, 1878. This image from the original paper is reproduced from J.J. Thomson, *The Corpuscular Theory of Matter*, Archibald Constable, London, 1907, p. 111.

Table 7.1
J.J. Thomson's electron rings.

Number of electrons	*Rings*	*Number of electrons*	*Rings*
5	5	16	5 + 11
6	1 + 5	17	1 + 5 + 11
7	1 + 6	18	1 + 6 + 11
8	1 + 7	19	1 + 7 + 11
9	1 + 8	20	1 + 7 + 12
10	2 + 8	21	1 + 8 + 12

Based on J.J. Thomson, *The Corpuscular Theory of Matter*, Archibald Constable, London, 1907, pp. 109–110.

in an atom results in the formation of one electron ring in Thomson's account. A second ring begins to form once the number of electrons reaches six, although after this happens, new electrons continue to be added to the first ring, just as in the case of the floating needles and corks. On reaching 10 electrons, a new electron suddenly appears in the second ring, and on reaching 17 electrons, a third ring begins to form. In each case, the additional, or differentiating, electron is generally being added to an inner ring rather than to an outer one.

From a modern point of view, these electronic arrangements have little merit in chemical terms since they suggest a nonexistent analogy between, for example, element 5, boron, and element 16, sulfur. It would be expected that, since they are assigned five electrons in their outermost shells according to this scheme, boron and sulfur would display similar chemical properties, which is not in fact the case. But it would be a mistake to criticize Thomson on this point, since in 1904 he and his contemporaries were not aware of the number of electrons in any particular atom. Not until Henry Moseley's work with atomic numbers was published 10 years later would it become clear that the serial number of an element in the periodic table, its atomic number, corresponds to the number of positive charges in the atom. In proposing his new scheme of electron rings, J.J. Thomson was merely suggesting the plausibility of explaining periodicity through similarities in electronic structures among different elements, something that remains valid to this day.

Although Thomson's atomic model would soon be discarded by Rutherford when he introduced his nuclear model of the atom,[13] it did succeed in establishing two important concepts. One was that the electron held the key to chemical periodicity, and the other was the notion that the atoms of successive elements in the periodic table differ by the addition of a single electron. Both of these ideas were to become important aspects of Niels Bohr's atomic theory of periodicity, which would soon be published.

The Quantum Theory of the Atom

When Rutherford revived Perrin's and Nagaoka's planetary model of the atom following Hans Geiger and Ernest Marsden's alpha particle scattering experiments, he left the problem of the model's stability unresolved. According to James Clerk Maxwell's electromagnetic theory, any circulating charged body should lose energy through radiation, so the orbiting electrons would be expected to spiral into the nucleus. The nuclear model implied that any atom, and consequently all matter, would thus be unstable, contrary to the obvious facts of experience. Furthermore, Rutherford's model could not explain the discrete nature of the optical spectra of atoms that had been accurately recorded since the development of the spectroscope in 1859 and that had been used to identify many new elements.[14]

The pattern observed following the dispersion of light emitted from excited atoms is quite different from that of white light. Instead of a continuous spectrum ranging from red to violet frequencies, one observes a series of discrete lines of various colors. Some particular color frequencies are simply missing compared with the spectrum from a source of white light. The discrete nature of the spectrum in the case of atoms could not be explained by any of the atomic models that have been reviewed so far. In Rutherford's model, for example, the energies of the electrons are not restricted to particular values; consequently, all possible transition energies would be expected to occur, and the optical spectrum of any element would be continuous rather than discrete.

Both of these problems, the stability of atoms and the discrete nature of atomic spectra, were resolved by the Danish physicist Bohr (figure 7.2), who also provided the first successful explanation of the periodic system in terms of arrangements of electrons in the atom.[15] Bohr obtained a Ph.D. in theoretical physics of the study of metals before undertaking a one-year postdoctoral fellowship with Rutherford at Manchester. Although other physicists had begun to establish the quantum theory in physics, Bohr was the first to apply these ideas in the context of atomic physics.

Bohr first came to prominence in 1913 when he published his quantum theory of the hydrogen atom. The notion of quanta, or packets of energy, had been introduced by Max Planck in 1900 to explain the details of observations made on black-body radiation.[16] Bohr adopted Planck's notion of quantization[17] and applied it to the physics of atoms. His calculations led him to conclude that, in the planetary model of the atom, additional rings of electrons are formed outside already full rings, correcting Thomson's model of electron rings, in which electrons are added to inner rings. Most important, Bohr proposed that electrons would be stable if they remained in certain quantized orbits, and they would lose energy only on undergoing transitions from one orbit to another, more stable orbit.[18] Electrons in a discrete set of stable orbits around the nucleus of an atom were said to be in stationary states that would not radiate energy:[19]

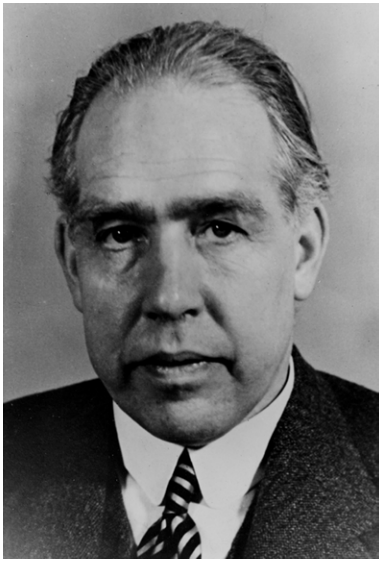


FIGURE 7.2
Niels Bohr. Photo and permission from Emilio Segrè Collection.

> An atomic system can only exist permanently in certain series of states corresponding to a discontinuous series of values for its energy, and that consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states are denoted as "stationary states" of the system.[20]

Bohr was following Planck's lead in departing from classical electromagnetic theory. In studying black-body radiation, which occurs at very short frequencies, Planck had found it necessary to introduce a constant, h, also called the elementary quantum of action, to explain its discontinuous nature. Such radiation could be emitted or absorbed only in packets, or quanta, described by the formula $h\nu$, where ν is the frequency of the radiation and h is Planck's constant. Bohr was suggesting that the atom could likewise not be described adequately by the laws of classical mechanics but that it required a quantum description.

Applying Planck's idea of how electrons move from one stationary state to another, Bohr proposed that for the atom to pass from one energy state to another it must emit or absorb one quantum, $h\nu$, of energy:

> The radiation absorbed or emitted during a transition between two stationary states is "unifrequentic" and possesses a frequency ν given by the relationship,
>
> $$E' - E = h\nu$$

where h is Planck's constant, and E' and E are the values of the energy in the two states under consideration.[21]

But this theory was limited in its application in that it gave an exact account only of the spectrum of hydrogen, the simplest case.[22] Atoms with more than one electron are much more complicated, since the various electrons exert influences on each other. Nevertheless, Bohr had sufficient confidence in his quantum theory of the atom to try to apply it to multielectron atoms in an approximate manner.

Although he first applied his quantum theory of the atom to the spectrum of the hydrogen atom, historians of physics John Heilbron and Thomas Kuhn have shown rather conclusively that the initial motivation for Bohr's theory was more comprehensive. Bohr was, rather, attempting to gain an understanding of the periodic table through electronic configurations[23] and to examine the stability of the electron rings with which Thomson had tried to explain the periodic table. In this same article of 1913, Bohr produced his first version of an electronic periodic table.[24] He assigned electronic configurations to the atoms of various elements in terms of the principal quantum number of each electron, which could be used to characterize its stationary or nonradiating states (table 7.2).

Bohr's general method, called the *aufbauprinzip* (German: building up), consisted in building up atoms of successive elements in the periodic table by the addition of an electron to the previous atom. On moving from one element to the next in the periodic table, Bohr supposed that an additional electron was added to the outermost shell, although there were exceptions to this rule, as discussed below. At specific stages in this process, a shell would become full, at which point a new shell would begin to fill. Contrary to the impression that he created in his published articles, however, Bohr was unable to deduce the maximum capacity of each electron shell, and he allowed himself to be guided almost entirely by chemical and spectroscopic data rather than theoretical calculations.

The fact that Bohr used essentially chemical considerations in producing these configurations can be seen clearly in his choice of configuration for certain elements. The population of electrons in the outermost ring is determined by chemical valence. These electrons are the most loosely bound to the nucleus and thus the most likely to bond with another atom. In the case of nitrogen, for example, Bohr was forced to rearrange an inner shell in order to make the configuration correspond to the element's known trivalence. This can be seen in table 7.2. Whereas from helium to carbon the atoms have two inner electrons and a varying number of outer electrons, once nitrogen is reached, the inner electron shell abruptly doubles in its number of electrons. This move appears a little odd until it is realized that it is made precisely to obtain the three outer electrons needed to correspond with the fact that nitrogen forms three chemical bonds.

In altering his configurations to make them agree with experimental evidence, Bohr gave no theoretical arguments for why such a rearrangement should occur.[25] Such abrupt rearrangements can be seen in a number of places, even among just the 24 configurations shown in table 7.2, such as for the atoms of nitrogen and phosphorus. The atoms of both of these elements show valences of 3, while oxygen

Table 7.2

Bohr's original scheme for electronic configurations of atoms. Numbers of electrons in consecutive energy levels, beginning closest to the nucleus.

1	H	1				
2	He	2				
3	Li	2	1			
4	Be	2	2			
5	B	2	3			
6	C	2	4			
7	N	4	3			
8	O	4	2	2		
9	F	4	4	1		
10	Ne	8	2			
11	Na	8	2	1		
12	Mg	8	2	2		
13	Al	8	2	3		
14	Si	8	2	4		
15	P	8	4	3		
16	S	8	4	2	2	
17	Cl	8	4	4	1	
18	Ar	8	8	2		
19	K	8	8	2	1	
20	Ca	8	8	2	2	
21	Sc	8	8	2	3	
22	Ti	8	8	2	4	
23	V	8	8	4	3	
24	Cr	8	8	4	2	2

N. Bohr, On the Constitution of Atoms and Molecules *Philosophical Magazine*, 26, 476–502, 1913, 497.

and sulfur display valences of 2 and fluorine and chlorine display valences of 1, in accordance with the chosen configurations. Instead of rigorously deriving his atomic model from quantum theory, Bohr relied on intuition as well as spectroscopic and purely chemical considerations.[26]

Nevertheless, Bohr achieved two things with his theory. First, he introduced the important idea that the differentiating electron should, in most cases, occupy an outer shell and not an inner one, as Thomson had thought was the case. Second, in spite of some arbitrary aspects, Bohr's scheme provided at least some correlation between electronic configurations and chemical periodicity. For example, the configuration of lithium is 2, 1, while that of sodium, which lies in the same group chemically, is 8, 2, 1. Similarly, beryllium and magnesium, which are found together in group II of the periodic table, share the property of having two outer-shell electrons. This is the origin of the modern notion that atoms fall into the same group of the periodic table if they possess the same number of outer-shell electrons, something that had already been hinted at by Thomson.[27]

Following this work, Bohr abandoned the question of periodicity for about a decade, and it was left to various chemists to try to improve upon the electronic version of the periodic table.[28] As discussed in chapter 8, there are some grounds for thinking that Bohr's later tables were directly influenced by the more detailed electronic configurations given by the chemist Charles Bury and that insufficient credit has been given to this pioneer of electronic configurations.

Bohr's Second Theory of the Periodic System

In 1921, Bohr returned to the problem of atomic structure and the periodic table. In 1922 and 1923, he announced a new, improved version of the electronic periodic table.[29] Again he employed the *aufbauprinzip* to build up successive atoms in the periodic table, but this time he used two quantum numbers: n, the principal quantum number, and k, the second or azimuthal quantum number, which later became labeled as ℓ (table 7.3). The second quantum number had recently been discovered by Arnold Sommerfeld, a theoretical physicist in Munich.

Whereas Bohr had assumed the orbit of the hydrogen electron to be circular, Sommerfeld realized that it was elliptical. Since the angular momentum of an electron moving in an elliptical orbit would change continually, the orbit itself would precess, independently of the motion of the electron in its ellipse. Thus, the electron would have two degrees of freedom: the orbiting motion of the electron and its precession. To describe the latter motion, Sommerfeld introduced a second quantum number, ℓ, the azimuthal quantum number, which depended on the principal quantum number and could adopt values of $n - 1, n - 2, \ldots, 0$.

When Bohr became aware of this discovery, he applied it to many-electron atoms and produced the set of more detailed electronic configurations shown in table 7.3. These numbers emerged from the quantization that was imposed mathematically on the system and served to identify the stationary states of the system, as they had in his earlier theory. According to this scheme, an atom of nitrogen, for example, with seven electrons, would have an electronic configuration of 2, 4, 1. It is interesting to see that in the case of nitrogen and a few other elements, Bohr's more detailed theory of 1922 seems to have taken a retrograde step, since contrary to the configuration he had given in 1913, the newer version did not accord well with the experimental fact that nitrogen forms three chemical bonds, a point taken up further below.

Table 7.3

Bohr's 1923 electronic configurations based on two quantum numbers. Numbers of electrons in consecutive energy levels, beginning closest to the nucleus.

H	1				
He	2				
Li	2	1			
Be	2	2			
B	2	3			
C	2	4			
N	2	4	1		
O	2	4	2		
F	2	4	3		
Ne	2	4	4		
Na	2	4	4	1	
Mg	2	4	4	2	
Al	2	4	4	2	1
Si	2	4	4	4	
P	2	4	4	4	1
S	2	4	4	4	2
Cl	2	4	4	4	3
Ar	2	4	4	4	4

N. Bohr, Linienspektren und Atombau, *Annalen der Physik*, 71, 228- 288, 1923, p. 260.

Following the early success of his theory of the hydrogen atom, Bohr was invited to give a series of seven lectures in 1922 at the University of Göttingen. Some of the physicists present in the audience for these lectures, which became known as the Bohrfest, included Werner Heisenberg, Wolfgang Pauli, Sommerfeld, and Max Born as well as Göttingen's leading mathematical physicist, David Hilbert. Throughout his career, Bohr was regarded more for his physical insight and his ability to synthesize ideas in atomic physics than for any special mathematical prowess, which he left to others like Werner Heisenberg Erwin Schrödinger, Wolfgang Pauli, and Paul Dirac. This lack of a formal mathematical approach was evident in Bohr's lectures at Göttingen, which produced questions from the audience regarding the mathematical justification for what Bohr was doing. It would appear that in many cases there were no such justifications.

As several of the Göttingen physicists who were exposed to these ideas by Bohr's own lectures later commented, the work rested on a mixture of ad hoc arguments and chemical facts without any derivations from the principles of quantum theory, to which Bohr frequently alluded. According to the German physicist Heisenberg,

> It could very distinctly be felt that Bohr had not reached his results through calculations and proofs but through empathy and inspiration and it was now difficult for him to defend them in front of the advanced school of mathematics in Göttingen.[30]

Friedrich Hund wrote:

> After he had explained a simple spectrum he came to his crucial review of the structure of atoms with regard to their positions in the periodic system. In some respects this turned out to be obscure and not always easy to understand.[31]

In a book containing Bohr's famous 1923 paper on the *aufbauprinzip*, Pauli made a revealing marginal remark. In discussing the addition of the 11th electron to the closed shell of 10 electrons, Bohr said, "We must expect the eleventh electron to go into the third orbit." Pauli, obviously annoyed by this statement, wrote hastily in the margin with an exclamation mark, "How do you know this? You only get it from the very spectra you are trying to explain!"[32] The notion that the periodic table was deduced from quantum theory by Bohr is thus something of an exaggeration.

Bohr claimed that his *aufbauprinzip*, by which he applied his theory of the atom to multielectron atoms, was based on an important principle of quantum theory called the adiabatic principle:[33]

> Suppose that for some class of motions we for the first time, introduce the quanta. In some cases the hypothesis fixes completely which special motions are to be considered as allowed. This occurs if the new class of motions are derived by means of an adiabatic transformation from some class of motions already known.[34]

Introduced by Paul Ehrenfest in 1917, the adiabatic principle allows one to find the quantum conditions when an adiabatic or gradual change is imposed on a system.[35] However, it depends on the possibility of deriving the new motion from the known one by means of an adiabatic transformation. For example, if the quantum states of a particular system are known, the new quantum states that result from a gradual change, such as the application of an electric or a magnetic field, can be calculated. The quantities that preserve their values after such a transformation are known as adiabatic invariants. Ehrenfest showed that for any arbitrary periodic motion, the following quantity is an adiabatic invariant:

$$2T/n,$$

where T is the time average of the kinetic energy and n is the frequency of motion.

There are stringent restrictions on the applicability of the adiabatic principle. Ehrenfest himself showed that it was applicable to simply periodic systems.[36] These are systems having two or more frequencies that are rational fractions of each other. In such systems, the motion will necessarily repeat itself after a fixed interval of time. Later, J.M. Burgers, a student of Ehrenfest, showed that it was also applicable to multiply periodic systems.[37] In these more general systems, the various frequencies are not rational fractions of each other, such that the motion does not necessarily repeat itself.[38] The hydrogen atom provides an example of a multiply periodic system, with its two degrees of freedom.

An even more general class of systems is termed aperiodic, and as far as is known, the adiabatic principle does not apply in such cases. Unfortunately for the field of atomic physics, all atoms larger than that of hydrogen constitute aperiodic systems. In the helium atom, for example, the motion of each of the two orbiting electrons changes according to the varying interaction with the other electron as their distance apart changes (in terms of the early Bohr theory). We may no longer speak of a constant period for either of the electrons.

Bohr was well aware of this limitation of the adiabatic principle but continued to use it even for many-electron atoms in the hope that it might still remain valid for such aperiodic systems. He repeatedly acknowledged this point in his writings:

> For the purposes of fixing the stationary states we have up to this point only considered simply or multiply periodic systems. However the general solution of the equations frequently yield motions of a more complicated character. In such a case the considerations previously discussed are not consistent with the existence and stability of stationary states whose energy is fixed with the same exactness as in multiply periodic systems. But now in order to give an account of the properties of the elements, we are forced to assume that the atoms, in the absence of external forces at any rate always possess sharp stationary states, although the general solution of the equations of motion for the atoms with several electrons exhibits no simple periodic properties of the type mentioned.[39]

Later, in his 1923 article, he states:

> We shall try to show that not withstanding the uncertainty which the preceding conditions contain, it yet seems possible even for atoms with several electrons to characterize their motion in a rational manner by the introduction of quantum numbers. The demand for the presence of sharp, stable, stationary states can be referred to in the language of quantum theory as a general principle of the existence and permanence of quantum numbers.[40]

Bohr's attitude as expressed in these writings does not seem to be very rigorous, but more akin to the obscurantism that characterized some of his scientific work.[41] In the two above-quoted passages he appears to ignore the problems he himself elaborates and merely expresses the hope of retaining the quantum numbers, even though one is no longer dealing with multiply periodic systems.

The main feature of the building-up procedure, as mentioned above, was Bohr's assumption that the stationary states would also exist in the next atom in the periodic table, obtained by the addition of a further electron. Bohr also assumed that the number of stationary states would remain unchanged from the atom of one element to the next, apart from any additional states pertaining to the newly introduced electron. He thus envisaged the existence of sharp stationary states and their retention on adding both an electron and a proton to an atom.

Bohr's hypothesis of the permanence of quantum numbers came under attack from the analysis of the spectral lines under the influence of a magnetic field.[42] As is generally the case, the application of a magnetic field on the atoms results in a splitting, to produce more lines than occur in the absence of such a field. An atomic core consisting of the nucleus and inner-shell electrons showed a total of N spectroscopic terms in a magnetic field. If an additional electron having an azimuthal quantum number k were to be added, the new composite system would be expected to show $N(2k-1)$ states, since the additional electron was associated with $2k-1$ states. However, experiments revealed more terms. In general, the terms split into one type consisting of $(N+1)(2k-1)$ components and a second type consisting of $(N-1)(2k-1)$ components, giving a total number of $2N(2k-1)$ components. This represents a violation of the number of quantum states, since a twofold increase seems to occur in the number of atomic states on the introduction of an additional electron. Bohr's response was to maintain adherence to the permanence of quantum numbers even in the face of this evidence. He merely alluded to a mysterious device, which he called a nonmechanical "constraint," to save the quantum numbers.[43]

Bohr's account of the periodic table also came under attack from chemical evidence. The element nitrogen, for example, was attributed an electronic configuration of 2, 4, 1, as noted above. This grouping of electrons suggested that one or five electrons were more loosely bound than the others and implied either penta- or univalence, neither of which is the case in practice, as nitrogen is predominantly trivalent.

Despite the problems with his quantum theory, Bohr went on to make numerous other contributions to atomic physics and quantum mechanics in the course of his long life. Indeed, Bohr is probably the best-known physicist of the twentieth century, eclipsed only by Albert Einstein. After Bohr's theories of 1913 and 1922–1923, he remained at the heart of developments in quantum theory, although specific steps were often taken by others, including Heisenberg, Schrödinger, and Pauli. But throughout this period, and for many years later, Bohr played the role of godfather to quantum theory by founding an international institute in Copenhagen, which hosted many of the world's leading physicists as they continued to shape the new quantum mechanics. In addition, he served as the focal point for discussions on the nature of quantum mechanics and had a profound influence on many of the physicists of his generation through his willingness to engage in debate.[44]

Edmund Stoner

Shortly after introducing his second theory of the periodic system, Bohr began to believe that the assumptions on which it was based might be unfounded, but it was not until the work of Pauli a little later that the situation would begin to be clarified. In the meantime, another physicist, Edmund Stoner, was to provide the next missing piece of the puzzle of quantum numbers and the periodic table.

In 1924, British-born Stoner (figure 7.3), then a graduate student at Cambridge University, took the next step in using electronic configurations to explain the periodic table.[45] His approach was based on using not merely two quantum numbers, but also a third one introduced by Sommerfeld shortly before.[46] The third, or inner, quantum number, j, refers to the precession of the orbital motion in the presence of a magnetic field. Its value is tied to the second quantum number such that j can take all values ranging from $-k$ to $+k$, increasing in integral steps.[47]

The occurrence of this third quantum number suggested additional stationary states in the atom, but Bohr did not extend his electronic configuration scheme accordingly. As mentioned above, Bohr was becoming increasingly interested in the deeper question of the existence of stationary states for individual electrons in

FIGURE 7.3
Edmund Stoner. Photo and permission from University of Leeds.

TABLE 7.4
Stoner's scheme for assignment of electronic configurations.

n	*k*	*j*	*Number of electrons*
1	1	1	2
2	1	1	2
2	2	1	2
2	2	2	4
3	1	1	2
3	2	1	2
3	2	2	4

Based on E. Stoner, The Distribution of Electrons Among Atomic Levels, *Philosophical Magazine*, 48, 719–736, 1924, p. 720.

many-electron atoms. That is, he was concerned about the fact that, strictly speaking, the electrons in many-electron atoms are not in stationary states. It is rather the atom as a whole that possesses stationary states. This "holistic" property denies the validity of the independent electron approximation wherein each electron is in a stationary state and can be characterized by its own set of quantum numbers.[48]

The young Stoner, undaunted by these theoretical problems, reexamined the experimental evidence on optical as well as X-ray spectra of atoms. Based on his studies, he suggested that the number of electrons in each completed level should equal twice the inner quantum number of that particular shell. This produced the scheme shown in table 7.4 for ascribing electrons to shells.

When Stoner applied this relationship to the three quantum numbers, he deduced the set of electron configurations shown in table 7.5. According to Stoner's scheme, the electronic configuration for the element nitrogen is 2, 2, 2, 1, where the last three numbers represent the outer-shell electrons. This configuration could account successfully for the valence state of 3 shown by nitrogen, whereas Bohr's scheme could not. However, this new scheme could not resolve the above-mentioned problem of the violation of number of quantum states, as was seen in the splitting of spectral lines in a magnetic field.

As the problems with what became known as Bohr's "old quantum theory" began to deepen, some physicists, such as Heisenberg and Pauli, started to question the reality of electron orbits. For example, in Pauli's correspondence with Bohr there is the following passage on this issue: "The most important question seems to be this: to what extent may definite orbits in the sense of electrons in stationary states be spoken of at all."[49]

Table 7.5
Stoner's configurations of 1924 based on three quantum numbers.

	Numbers of electrons in successive energy levels beginning closest to the nucleus.						
H	1						
He	2						
Li	2	1					
Be	2	2					
B	2	2	1				
C	2	2	2				
N	2	2	2	1			
O	2	2	2	2			
F	2	2	2	3			
Ne	2	2	2	4			
Na	2	2	2	4	1		
Mg	2	2	2	4	2		
Al	2	2	2	4	2	1	
Si	2	2	2	4	2	2	
P	2	2	2	4	2	2	1
S	2	2	2	4	2	2	2
Cl	2	2	2	4	2	2	3
Ar	2	2	2	4	2	2	4

Based on E. Stoner, The Distribution of Electrons Among Atomic Levels, *Philosophical Magazine*, 48, 719–736, 1924, p. 734.

The Pauli Exclusion Principle

In 1923, Bohr wrote to Pauli (figure 7.4), asking him to try to bring order to the increasingly complicated situation in atomic physics[50] and to attempt to save the quantum numbers. Pauli responded with two papers that seemed to clarify matters, and in the process he developed his exclusion principle, which has become one of the central pillars of modern physics. Once again, the motivation for this work was partly an attempt to explain the periodic table of the elements.

Pauli's first main contribution was to challenge the view held at the time that the core of an atom possesses an angular momentum.[51] Alfred Landé[52] had proposed that the core of the atom, consisting of the nucleus plus the inner electrons, would explain the origin of the complex structure of atomic spectra. Pauli rejected this hypothesis and suggested that the spectral lines and their shifts in the presence of magnetic fields were due entirely to the presence of outer electrons. He went on to propose the assignment of a fourth quantum number, m_s, to each electron

FIGURE 7.4
Wolfgang Pauli. Photo from author's collection used by permission from Emilio Segrè Collection.

(table 7.6). This fourth number was due, according to Pauli, to a classically nondescribable duplicity in the quantum theoretical properties of the optically active electron,[53] a property now called spin angular momentum.

Armed with four quantum numbers, Pauli found that he could obtain Stoner's classification of electronic configurations from the following simple assumption, which constitutes the famous exclusion principle in its original form: "It should be forbidden for more than one electron with the same value of the main quantum number n to have the same value for the other three quantum numbers k, j and m."[54] The principle is often stated as follows: no two electrons in an atom can have the same set of four quantum numbers. Meanwhile, Pauli justified the assignment of four quantum numbers to each electron by the following apparently clever argument. He supposed that if a strong magnetic field were applied, the electrons would cease to interact and could therefore be said to be in individual stationary states.

Of course, the periodic table arrangement must also apply in the absence of a magnetic field. In order to maintain the validity of the four-quantum-number assignment for each electron even in the absence of a field, Pauli appealed to what he called a "thermodynamic argument." He proposed an adiabatic transformation in which the strength of the magnetic field was gradually reduced such that, even in the absence of the field, the characterization of stationary states for individual electrons remained valid. This argument seemed to ensure the existence of sharp stationary states for individual electrons.

TABLE 7.6

Assignment of electron shells based on Pauli's scheme.

n	ℓ	m_ℓ	m_s	Number of electrons
1	0	0	+1/2	
			–1/2	2
2	0	0	+1/2	
			–1/2	2
2	1	–1	+1/2	
			–1/2	2
2	1	0	+1/2	
			–1/2	2
2	1	1	+1/2	
			–1/2	2
3	0	0	+1/2	
			–1/2	2

Modern labels for the quantum numbers have been used instead of *k* and *j*. This does not alter any of the arguments presented here. Based on W. Pauli, On the Connexion between the Completion of Electron Groups in an Atom with the Complex Structure of Spectra *Zeitschrift für Physik*, 31, 765–783, 1925. The table shown uses modern labels for the four quantum numbers, not those used by Pauli.

Pauli then considered how this proposal fared with regard to the experimental evidence showing a violation in the number of quantum states. As mentioned above, the problem was that a system expected to show $N(2k - 1)$ states on the addition of a single electron to the atomic core is in fact transformed into two sets of states numbering $(N + 1)(2\ k - 1)$ and $(N - 1)(2k - 1)$ states, or a total of $2N(2k - 1)$.

Pauli was able to resolve this problem very simply. According to his view, the additional electron possesses $2(2k - 1)$ states, in contrast to the former view of only $(2k - 1)$. The twofold increase in the number of observed states arises from the proposed duplicity of states of the new electron. The number of states of the atomic core therefore remains as N. Pauli's arguments appeared very persuasive and were received enthusiastically by the atomic physics community.

Not surprisingly, Bohr was pleased with Pauli's contribution, although both of them seemed to view it as a temporary measure. What they and everybody else failed to notice was that Pauli had committed a fallacy concerning the applicability of the adiabatic principle. A many-electron atom constitutes an aperiodic system to which the adiabatic principle does not apply, as previously emphasized by Bohr. Pauli merely changed the argument from the addition of an extra electron as in the *aufbauprinzip* to the case of gradually reducing the strength of a magnetic field. This

TABLE 7.7
Quantum numbers and orbitals.

n	*Possible values of ℓ*	*Subshell designation*	*Values of* m_ℓ	*Number of Possible orbitals in subshell*
1	0	1s	0	1
2	0	2s	0	1
	1	2p	1, 0, –1	3
3	0	3s	0	1
	1	3p	1, 0, –1	3
	2	3d	2, 1, 0, –1, –2	5
4	0	4s	0	1
	1	4p	1, 0, –1	3
	2	4d	2, 1, 0, –1, –2	5
	3	4f	3, 2, 1, 0, –1, –2, –3	7

does not alter the issue, however, since the system remains aperiodic, and Pauli was using the adiabatic principle where it did not strictly apply. But as often happens in science, taking a step that is not rigorous can often pay dividends, at least temporarily, as it did in this case.

Perhaps the reason why theoretical considerations were suspended was that Pauli's new scheme resolved some major problems. First, the notion of the existence and permanence of the quantum numbers could be retained, as Bohr had hoped. Second, the long-standing problem of the "closing of electron shells" in atoms was resolved. The question had been how to explain the series of whole numbers 2, 8, 18, 32, and so on, which characterizes the lengths of the periods in the periodic system of chemical elements. These numbers also correspond to the maximum number of electrons in each shell. Now the closing of the various shells could be seen to be a consequence of Pauli's exclusion principle, which prohibits any two electrons from having the same four quantum numbers, together with the assumption that the fourth number itself can adopt only two possible values. Meanwhile, all the previous rules for assigning the values for the second and third quantum numbers for a given value of the first quantum number were retained.

When the first quantum number, or *n*, takes the value of 1, the second quantum number can only be 0, and likewise the third quantum number (table 7.7). According to Pauli's principle, the first shell can therefore contain a maximum number of two electrons that differ just in the value of the fourth quantum number.

For the $n = 2$ shell, the situation is more complicated, since there are two possible values for the second quantum number: 0 and 1. As noted above, when the second quantum number is 0, the third quantum number also adopts a 0 value and, since the fourth quantum number can adopt two possible values, two electrons are accounted for. When the second quantum number in the second shell takes a value of 1, the third quantum number may take on three possible values: – 1, 0, and +1. Each of these possibilities can show two values for the fourth quantum number, thus accounting for a further six electrons. Considering the second shell as a whole, a total of eight electrons is therefore predicted, in accordance with the well-known short period length of eight elements.

Similar considerations for the third and fourth shells predict 18 and 32 electrons, respectively, once again in accordance with the arrangement of the elements in the periodic table.

This scheme is still widely regarded as the explanation for the periodic table, and some version of it is found in virtually every textbook in chemistry or physics. But it is only a partial explanation. It relies for its success on using experimentally observed data in order to determine at what point, in the sequence of the elements, any particular electron shell begins to be filled. The explanation provided by Pauli and most textbooks is only an explanation of the maximum number of electrons successive electron shells can accommodate. It does not explain the particular places in the periodic table at which periodicity occurs. This is to say that Pauli's explanation alone does not explain the lengths of *periods*, which is the really crucial property of the periodic table.

The more important aspect of the periodic system, namely, the lengths of the periods and their explanation, is taken up again in chapter 9. Just to anticipate matters a little, it will emerge that even present-day physics has not provided a deductive explanation of the closing of the periods, although some promising candidate explanations are becoming available. This situation is seldom acknowledged in textbooks or even in the research literature. Such sources give the impression that quantum physics provides a fully deductive explanation of the closing of the periods, or the particular atomic numbers at which each period is terminated.

Notes

1. As mentioned in chapter 6, the notion that Thomson alone discovered the electron is hotly debated among historians of science.

2. M. Chayut, J.J Thomson, The Discovery of the Electron and the Chemists, *Annals of Science*, 48, 527–544, 1991.

3. There has been debate in the literature regarding the extent to which chemical or physical atomism was supported by various developments starting from John Dalton's theory. See, e.g., A. Chalmers, *The Scientist's Atom and the Philosopher's Stone*, Springer, Berlin, 2009.

4. As cited in A. Pais, *Inward Bound*, Clarendon Press, Oxford, 1986, p. 82.

5. Contrary to Thomson's original finding of a charge-to-mass ratio of 770 for cathode rays emanating from hydrogen ions, the electron was found to have a mass of 1836 times less than that of the hydrogen atom.

6. J. Perrin, Les Hypotheses Moleculaires, *Revue Scientifique*, 15, 449–461, 1901.

7. Ibid., quoted from p. 460.

8. The concept of electron orbitals, or the earlier notion of electron orbits, began with Niels Bohr's theory of the atom, which is examined further below. Electronic orbitals have become perhaps the most important concept in the modern explanation of the periodic system, as discussed in chapters 8–10.

9. H. Nagaoka, Motion of Particles in an Ideal Atom Illustrating the Line and Band Spectra and the Phenomena of Radioactivity, *Bulletin of the Mathematics and Physics Society of Tokyo*, 2, 140–141, 1904.

10. H. Nagaoka, Kinetics of a System of Particles Illustrating the Line and the band Spectrum and the Phenomena of Radioactivity, *Philosophical Magazine*, 7, 445–455, 1905.

11. J.J. Thomson, On the Structure of the Atom: An Investigation of the Stability and Periods of Oscillation of a Number of Corpuscles Arranged at Equal Intervals around the Circumference of a Circle; with Application of the Results to the Theory of Atomic Structure, *Philosophical Magazine*, 7, 237–265, 1904.

12. A.M. Meyer, A Note on Experiments with Floating Magnets, *American Journal of Physics*, 15, 276–277, 1878.

13. Rutherford described Thomson's plum pudding model as being like old lumber fit only for a museum of scientific curiosities.

14. Optical spectra result from outer or valence electrons and should not be confused with the spectra obtained by Moseley using an X-ray source rather than visible light. X-ray spectra involve the excitation of inner electrons.

15. Another underrated contributor to this project was the British physicist John Nicholson. See T. Rothman, *Everything's Relative*, Wiley, Hoboken, NJ, 2003. Also see E.R. Scerri, *A Tale of Seven Scientists*, Oxford University Press, New York, 2016, chapter 2.

16. Experiments on incandescent objects inside a perfectly absorbing cavity produced a set of spectral distributions depending on the temperature of the heated object and the wavelength of light emitted by the object. The classical theory available to describe these spectral distributions appeared to be applicable only at high wavelengths; at lower wavelengths, the theory predicted infinite emission intensities for the same heated objects, which did not agree with the experimental facts. Planck succeeded in explaining the experimental curves by assuming that, contrary to previous thinking, the energy of particles in the heated object, and consequently the energy emitted in such experiments, is not continuous but in the form of discrete units.

17. Strictly speaking, Planck's work revealed the quantization of "action," that is to say, energy divided by frequency. This quantity is now of historical interest only, and it is more common to refer to the quantization of energy, which is given by the action of a particular system multiplied by its frequency.

18. Conversely, electrons could undergo transitions to less stable orbits following the absorption of specific quanta of energy.

19. As many authors note, the quantization of angular momentum assumed by Bohr as well as the notion that electrons in stationary states do not radiate was somewhat ad hoc and only justified later by Erwin Schrödinger's approach to calculating the energy of the hydrogen atom.

20. N. Bohr, On the Constitution of Atoms and Molecules, Part III. Systems Containing Several Nuceli, *Philosophical Magazine*, 26, 857–875, 1913. Quoted from p. 874.

21. Ibid., quoted from p. 875.

22. Bohr's atomic theory also provided an approximate explanation for the spectra of alkali metals, which have one unpaired outer-shell electron.

23. J.L. Heilbron, T.S. Kuhn, The Genesis of the Bohr Atom, *Historical Studies in the Physical Sciences*, 1, 211–290, 1969.

24. N. Bohr, On the Constitution of Atoms and Molecules, *Philosophical Magazine*, 26, 476–502, 1913, table on p. 497.

25. E.R. Scerri, Prediction of the Nature of Hafnium from Chemistry from Chemistry, Bohr's Theory and Quantum Theory, *Annals of Science*, 51, 137–150, 1994.

26. For discussions of how Bohr argued as a chemist, see H. Kragh, Chemical Aspects of Bohr's 1913 Theory, *Journal of Chemical Education*, 54, 208–210, 1977.

27. This statement is a simplification and is only correct for the main-group, or representative, elements in the periodic table. In the case of the transition elements, the members of a group of elements have the same number of electrons in the same penultimate shell. In the rare earths, the elements in the same group have the same number of electrons in a shell located two shells from the outer shell. And there are further deviations, given that about 20 elements have "anomalous" configurations, as discussed in chapter 9.

28. I. Langmuir, Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 41, 868–934, 1919; C.R. Bury, Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 43, 1602–1609, 1921.

29. N. Bohr, Über die Anwendung der Quantumtheorie auf den Atombau. I. Die Grundpostulate der Quantumtheorie, *Zeitschrift für Physik*, 13, 117–165, 1923, English translation in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 3, North-Holland Publishing, Amsterdam, 1981.

30. Quoted in H. Kragh, The Theory of the Periodic System, in A.P. French, P.J. Kennedy (eds.), *Niels Bohr, A Centenary Volume*, Harvard University Press, Cambridge, MA, 1985, 50–67, quoted from p. 61.

31. Quoted in J. Mehra, H. Rechenberg, *The Discovery of Quantum Mechanics, 1925*, vol. 2 of *Historical Development of Quantum Theory*, Springer-Verlag, New York, 1982.

32. Quoted in Victor F. Weisskopf, *The Privilege of Being a Physicist*, W.H. Freeman, New York, 1970, quoted from p. 164.

33. N. Bohr, Uber die Anwendung der Quantumtherie auf den Atombau I, *Zeitschrift für Physik*, 13, 117–165, 1923.

34. P. Ehrenfest, Adiabatic Invariants and the Theory of Quanta, *Philosophical Magazine*, 33, 500–513, 1917, quoted from p. 501.

35. The term "adiabatic" has a different sense in thermodynamics than it does in quantum mechanics. In thermodynamics, it refers to a change carried out very quickly so that the system in question does not undergo any heat change. In quantum mechanics, an adiabatic change must be gradual so that the quantum states of the system are maintained following the change.

36. P. Ehrenfest, Adiabatic Invariants and the Theory of Quanta, *Philosophical Magazine*, 33, 500–513, 1917.

37. J.M. Burgers, Adiabatic Invariants of Mechanical Systems, *Philosophical Magazine*, 33, 514–520, 1917.

38. H. Goldstein, *Classical Mechanics*, 2nd ed., Addison-Wesley, Reading, MA, 1980.

39. N. Bohr, Uber die Anwendung der Quantumtherie auf den Atombau I, *Zeitschrift für Physik*, 13, 117–165, 1923, quoted from p.129.

40. Ibid., quoted from p. 130.

41. J. Honner, Niels Bohr and the Mysticism of Nature, *Zygon*, 17, 243–253, 1982.

42. A. Landé, Termstruktur und Zeemaneffekt der Multipletts, *Zeitschrift für Physik*, 15, 189–205, 1923.

43. A. Sommerfeld, *Wave Mechanics*, E.P. Dutton, New York, 1930.

44. The 100th anniversary of Bohr's trilogy took place in 2013 and was marked by the publication of several books and articles, among which were F. Aaserud, J. Heilbron, *Love, Literature and the Quantum Atom*, Oxford University Press, Oxford, 2013; H. Kragh, *Niels Bohr and the Quantum Atom*, Oxford University Press, Oxford, 2012; W.H.E. Schwarz, 100th Anniversary of Bohr's Model of the Atom, *Angewandte Chemie International Edition*, 52 (47), 12228–12238, 2013.

45. See a chapter on Stoner in E.R. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016, 117–148.

46. E. Stoner, The Distribution of Electrons among Atomic Levels, *Philosophical Magazine*, 48, 719–736, 1924.

47. In modern notation, the third quantum number is labeled m_ℓ, and the second quantum number is ℓ. Thus, if $\ell = 2$, m_ℓ can take values of –2, –1, 0, +1, and +2. The second or ℓ quantum number, in turn, is related to the first quantum number n as $\ell = n - 1, \ldots 0$. E.g., if $n = 3$, m_ℓ can assume values of 2, 1, or 0.

48. For a philosophical discussion of the nature of atomic orbitals, see E.R. Scerri, *British Journal for the Philosophy of Science*, 42, 309–325, 1991; and response by Z. Jenkins, Do You Need to Believe in Orbitals to Use Them?: Realism and the Autonomy of Chemistry, *Philosophy of Science*, 70(5), 1052–1062, 2003.

49. W. Pauli, letter to N. Bohr, February 21, 1924, quoted in Bohr-Pauli Correspondence, *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 5, North-Holland Publishing, Amsterdam, 1981, Translation on pp. 412–414. This quotation is all the more remarkable because, as argued below, it was Pauli's own exclusion principle, formulated a few months later, that seemed to reinstate the notion of individual electrons in stationary states. The notion of individual electrons in individual stationary states was finally refuted with the advent of quantum mechanics. Only the atom as a whole possesses stationary states. The distinction is rather important for the physics of many-electron systems.

50. Complications included the occurrence of half quantum numbers, the problem of the anomalous Zeeman effect, and the doublet riddle. P. Forman, The Doublet Riddle and Atomic Physics *circa* 1924, *Isis*, 59, 156–174, 1968.

51. W. Pauli, Über den Einfluss der Geschwindigkeitsabhängigkeit der Elektronmasse auf den Zeemaneffekt, *Zeitschrift für Physik*, 31, 373–385, 1925.

52. A. Landé, Termstruktur und Zeemaneffekt der Multipletts, *Zeitschrift für Physik*, 15, 189–205, 1923.

53. W. Pauli, Über den Zusammenhang des Abschlusses der Elektrongruppen im Atom mit Complexstruktur der Spektren, *Zeitschrift für Physik,* 31, 765–783, 1925, quoted from p. 765.

54. Ibid., quoted from p. 778.

CHAPTER

8

ELECTRONIC EXPLANATIONS OF THE PERIODIC SYSTEM DEVELOPED BY CHEMISTS

Given the advances in explanations of the periodic system provided by physicists in the first quarter of the twentieth century, described in chapter 7, it is interesting to consider what advances, if any, chemists achieved during the same period. Unlike physicists, chemists were working largely inductively with experimental data on the elements and not via any theoretical arguments.

However, in many instances, the electronic configurations proposed by chemists were superior to those postulated by such physicists as Niels Bohr and Edmund Stoner. This is not entirely surprising given the chemist's familiarity with the properties of the elements. Inductive arguments based on the macroscopic behavior of elements were often more fruitful than the deductive arguments based on physical principles. Moreover, as described in chapter 7, even physicists' routes to electronic configurations were not always as deductive as their authors claimed them to be.

The starting point for the chemical contributions to the assignment of electronic configurations can be regarded as J.J. Thomson's discovery of the electron in 1897, since without the existence of this particle there could be no electronic configurations. In 1902, the American chemist Gilbert Norton Lewis (figure 8.1) began speculating about the electronic structure of atoms, although he did not publish his views due to the prevailing empiricist climate in US chemistry, which was rather hostile toward theoretical approaches.[1] Considerably later, Lewis recalled his early thoughts on the constitution of atoms:

> In the year 1902 (while I was attempting to explain to an elementary class in chemistry some of the ideas involved in the periodic law) becoming interested in the new theory of the electron, and combining this idea with those implied in the periodic classification, I formed an idea of the inner structure of the atom which, although it contained certain crudities, I have ever since regarded as representing essentially the arrangement of electrons in the atom.

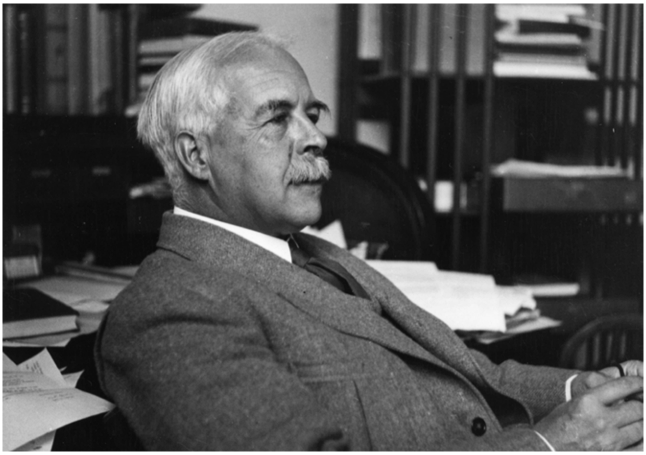


FIGURE 8.1 Gilbert Norton Lewis. Photo and permission from Edgar Fahs Smith Collection.

Some dated fragments of this work still survive, including a diagram in which Lewis depicts the electronic structures of the elements from helium up to fluorine (figure 8.2). Lewis envisaged the electrons as being arranged at the corners of a cube, and he observed that when the number eight was exceeded, another cube would be formed to build up a series of concentric cubes around the nucleus of any element.

It should be realized that from purely chemical evidence Lewis had succeeded in deducing the correct number of electrons for all but one (helium) of the first dozen or so elements in the periodic system, whereas, as discussed in chapter 7, this had been a major stumbling block for the physicist Thomson.[2] The latter's electronic account of the periodic table showed only that it might be possible to relate elements in the same group in terms of analogous configurations. Lewis succeeded in explaining the formation of polar or, as more commonly termed, ionic compounds such as sodium chloride by means of his cubic atom concept. According to his model, the sodium atom, which possessed one electron on the corner of a cube, could lose this electron to form a positive sodium ion with no outer electrons on any of the corners. Meanwhile, the cube around a chlorine atom would begin with seven of its eight corners occupied with electrons and would gain the spare electron from sodium. This would give the chlorine a full complement of eight electrons, thereby forming a negative chlorine ion, which would be attracted to the positive sodium ion.

While this model could explain the formation of polar compounds, it could not address how nonpolar organic compounds, such as methane, might be formed. This serious limitation may have been another reason why Lewis did not publish his early ideas on the cubic atom. It was only in 1916 that Lewis did so. These ideas on the cubic atom and pairs of electrons were to lead Lewis to formulate one of the most influential ideas in the whole of modern chemistry: the notion of a

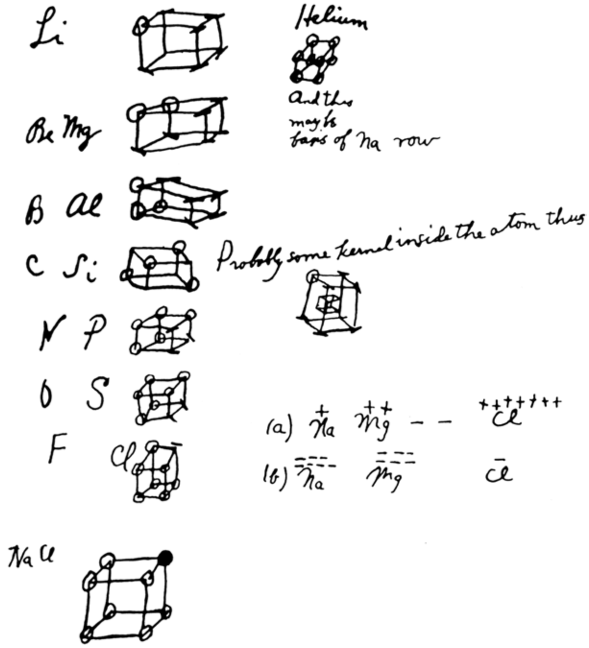


FIGURE 8.2 Lewis's sketch in his unpublished memorandum of March 28, 1902. Lewis Archive, University of California, Berkeley.

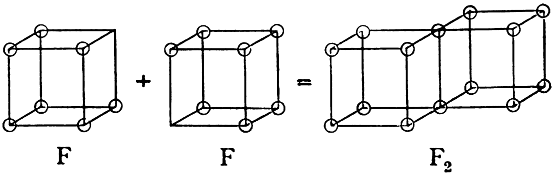


FIGURE 8.3 The formation of a covalent bond between cubes representing fluorine atoms. Reproduced from A. Stranges, *Electrons and Valence*, Texas A&M University Press, College Station, TX, 1982, p. 212, with permission from the publisher.

covalent bond as a shared pair of electrons. Until this time, chemical bonds had been regarded exclusively as involving the transfer of electrons and the formation of ionic bonds.[3] It is interesting to realize that the concept of a covalent bond thus began, like so many important developments in modern science, with research connected to the periodic system of the elements. Moreover, Lewis's 1916 article, titled "The Atom and the Molecule," has turned out to be one of the most influential works in modern chemistry.[4] What Lewis also suggested was that the two kinds of bonding were essentially forms of the same behavior, namely, the sharing of electrons between atoms. In the case of polar compounds, this sharing could be regarded as being very uneven, whereas in nonpolar compounds the electrons could be more or less equally shared by adjacent atoms of different elements.

In this chapter, I concentrate on what Lewis had to say on the periodic system and the structure of atoms. Lewis began by paying tribute to the work of German chemist Richard Abegg,[5] who in 1902 had proposed a rule of valence and contravalence:

> *The total between the maximum positive and negative valences of an element is frequently eight and in no cases more than eight.*

Abegg's maximum positive valence corresponds to the group number of the element in question in the periodic table. The normal valence is whichever of these two valences is less than four, while the contravalence, or "other valence," is displayed less commonly and gives rise to less stable compounds. The elements in group IV of the periodic table show no natural preference with respect to valency and were called amphoteric, a term that was first coined by Abegg and is still in chemical use today, although with a somewhat different meaning.[6]

Abegg explained why the sum of the valence and contravalence was eight by assuming that this number represented the number of electron attachment sites on any atom. However, he did not venture to speculate why each atom could attach precisely this number of electrons. This step was provided by Lewis, who devised his cubical atom on the basis of Abegg's rule. Each of the eight corners of a cube represented a site at which an electron could be attached. Indeed, whereas Abegg merely accepted the stability of eight electrons to an atom, for Lewis it was a simple consequence of the cubic structure of his hypothetical atom. As historian Anthony Stranges has suggested, Lewis's cubic atom appears to be a geometric representation of Abegg's arithmetical rule.[7]

Lewis gave a number of postulates:

1. In every atom is an essential kernel that remains unaltered in all ordinary chemical changes and that possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.
2. The atom is composed of a kernel and an outer atom or shell, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between zero and eight.
3. The atom tends to hold an even number of electrons in the shell and, especially, to hold eight electrons that are normally arranged at the eight corners of a cube.
4. Two atomic shells are mutually interpenetrable.
5. Electrons may ordinarily pass with readiness from one position in the outer shell to another. Nevertheless, they are held in position by more or less rigid

constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.

6. Electric forces between particles that are very close together do not obey the simple law of inverse squares that holds at greater distances.[8]

As a comment on postulate 3, Lewis points out that among the "tens of thousands of known compounds," only a few of them do not have an even number of electrons in their valence shells. In every compound in which the element uses either its highest or lowest valence, the total number of valence electrons is a multiple of eight. Examples given by Lewis include ammonia (NH_3), water (H_2O), and potassium hydroxide (KOH), all of which show a total of eight valence electrons, and magnesium chloride ($MgCl_2$), where the total is 16, and sodium nitrate ($NaNO_3$), where it is 24. The few exceptions to the notion of even numbers of valence electrons include NO (11), NO_2 (17), and ClO_2 (19), but Lewis adds that these molecules are highly reactive, forming more stable molecules where the number of valence electrons is once again even, such as in the case of the dimerization of NO_2 to form N_2O_4.

Postulate 4, which allows cubic atoms to interpenetrate, forms the basis of the electron sharing mechanism. In this way, one electron or more could belong to two atoms simultaneously without being gained or lost by either of the atoms. This simple idea, stemming directly from cubic arrangements of electrons, seems to be the origin of the now ubiquitous concept of electron sharing in chemistry. Lewis illustrated the interpenetration of cubes with the formation of a diatomic molecule held together by a single bond (figure 8.4). The concept could be extended to explain double bonds in such molecules as diatomic oxygen, which Lewis represented as two cubes sharing a common face (figure 8.5).

Postulate 6 implies an abandonment of Coulombic repulsion in the case of two closely lying electrons and is essential if one is to contemplate the existence of pairs of electrons as an integral part of the model. Interestingly, Lewis qualifies this postulate further by saying that electrons can act as small magnets that, when correctly oriented, can account for the stability of the shared pair of electrons.[9] This statement, and later elaborations, have been interpreted by many as an anticipation of

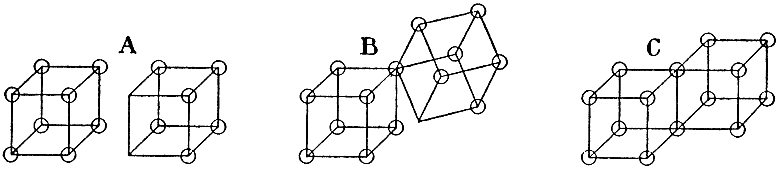


FIGURE 8.4 Single bond formation with cubic atoms. Reproduced from A. Stranges, *Electrons and Valence*, Texas A&M University Press, College Station, TX, 1982, p. 212, with permission from the publisher.

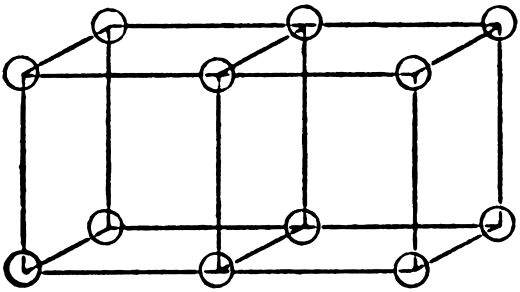


FIGURE 8.5 Double bond formation with cubic atoms. Reproduced from A. Stanges, *Electrons and Valence*, Texas A&M University Press, College Station, TX, 1982, p. 213, with permission from the publisher.

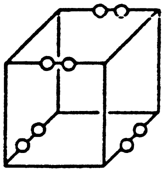


FIGURE 8.6
Lewis's tetrahedral atom. The electron pairs are now on the corners of a tetrahedron that has been superimposed on the earlier cubic structure.

the concept of electron spin, which, as discussed in chapter 7, was not formally introduced until 1925.[10]

What is curious about this article of 1916 is that Lewis begins with a detailed account of his cubic atom but in the very same article shows that it is necessary to go beyond this model. One of the shortcomings of the simple model is its inability to explain the formation of triple bonds such as in a molecule of ethyne (acetylene), with formula H–C≡C–H, or the diatomic nitrogen molecule N≡N. There seems to be no way that two cubes of electrons can share three pairs of electrons, and Lewis concludes that he needs to assume a somewhat different way of arranging the electrons in order to overcome this problem. The solution he offers is to place the electrons on the four corners of a tetrahedron that has been superimposed on the earlier cubic structure (figure 8.6). This new tetrahedral atom can accommodate the formation of a triple bond by assuming that two adjacent atoms share a common tetrahedral face.

Lewis's article also introduces the use of a pair of dots to denote the shared pair of electrons, a form of notation that survives to this day:[11]

$$\mathrm{H:Cl} \qquad \mathrm{H:H} \qquad \mathrm{Na:H}$$

Whereas in 1902 Lewis had thought that helium possessed a complete cube of eight electrons, he corrected its electronic structure in his 1916 paper to include just two electrons, as had been revealed by the work of Henry Moseley.[12] Table 8.1

TABLE 8.1
Lewis's outer electronic structures for 29 elements.

1	*2*	*3*	*4*	*5*	*6*	*7*
H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Sc		As	Se	Br
Rb	Sr			Sb	Te	I
Cs	Ba			Bi		

The number at the head of each column represents the positive charge on the atomic kernel and also the number of outer-shell electrons for each atom. Compiled by the author from G.N. Lewis,The Atom and the Molecule,*Jour- nal of the American Chemical Society*, 38, 762–785, 1916. Lewis does not give a table.

is based on the positive charges on the atomic kernels of a number of elements as given by Lewis in the same article.

Irving Langmuir

The next step in the evolution of chemically motivated electronic configurations was taken by another American, Irving Langmuir, who spent his life as an industrial research chemist and was responsible for making many of Lewis's ideas widely known.[13] In 1919, Langmuir published an article that begins with an insightful comment, especially in view of the kinds of questions raised in the present book, regarding the relationship between chemistry and physics in the evolution of the periodic system:

> The problem of the structure of atoms has been attacked mainly by physicists who have given little consideration to the chemical properties, which must ultimately be explained by a theory of atomic structure. The vast store of knowledge of chemical properties and relationships, such as is summarized in the periodic table, should serve as a better foundation for a theory of atomic structure than the relatively meager experimental data along purely physical lines.[14]

Langmuir remarks that Lewis confines his attention to only 35 of the 88 known elements and that his theory does not apply at all satisfactorily to the remaining elements, thus highlighting the limitations of Lewis's scheme especially for the transition elements. Langmuir then briefly reviews the work of Walther Kossel in which electrons are regarded as being in concentric rings, and he comments on the fact that while Kossel's theory considers elements up to cerium, that is, a total of 57 elements, just like Lewis's theory, it is unable to deal with the transition metals.[15]

Langmuir bases his own theory on the number of electrons in the atoms of the noble gases:

He = 2, Ne = 10, Ar = 18, Kr = 36, Xe = 54, niton[16] = 86

By means of "constant checking against the periodic table and the specific properties of the elements," Langmuir proceeds to elaborate seven postulates, which enable him to assign electronic configurations for all the naturally occurring elements up to uranium or $Z = 92$. He then provides a classification of the elements according to their arrangement of electrons in what is essentially a short-form periodic table in which the numbers of outer-shell electrons are displayed for each element along with their atomic number (figure 8.7).

Unlike Lewis, and Kossel before him, Langmuir does not hesitate to assign configurations to the transition element atoms. For example, the first transition series is depicted as follows:

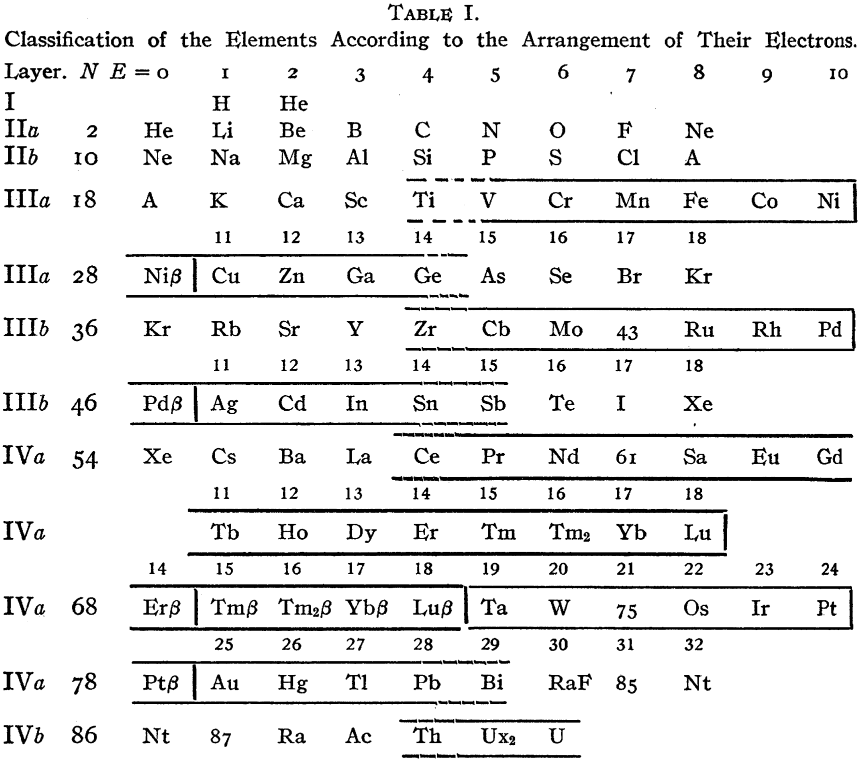


TABLE I.

Classification of the Elements According to the Arrangement of Their Electrons.

Layer.	N	E = 0	1	2	3	4	5	6	7	8	9	10
I			H	He								
IIa	2	He	Li	Be	B	C	N	O	F	Ne		
IIb	10	Ne	Na	Mg	Al	Si	P	S	Cl	A		
IIIa	18	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
			11	12	13	14	15	16	17	18		
IIIa	28	Niβ	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
IIIb	36	Kr	Rb	Sr	Y	Zr	Cb	Mo	43	Ru	Rh	Pd
			11	12	13	14	15	16	17	18		
IIIb	46	Pdβ	Ag	Cd	In	Sn	Sb	Te	I	Xe		
IVa	54	Xe	Cs	Ba	La	Ce	Pr	Nd	61	Sa	Eu	Gd
			11	12	13	14	15	16	17	18		
IVa			Tb	Ho	Dy	Er	Tm	Tm_2	Yb	Lu		
		14	15	16	17	18	19	20	21	22	23	24
IVa	68	Erβ	Tmβ	Tm_2β	Ybβ	Luβ	Ta	W	75	Os	Ir	Pt
			25	26	27	28	29	30	31	32		
IVa	78	Ptβ	Au	Hg	Tl	Pb	Bi	RaF	85	Nt		
IVb	86	Nt	87	Ra	Ac	Th	Ux_2	U				

FIGURE 8.7 Langmuir's periodic table of electronic configurations. W. Langmuir, Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 41, 868–934, 1919, p. 874.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3	4	5	6	7	8	9	10	11	12

where the numbers denote the number of outermost electrons.[17]

The 10th postulate given by Langmuir is significant for two reasons. First, it includes the statement that there can be no electrons in the outer shell of an atom until all the inner shells contain the maximum number of electrons that each one can accommodate. Second, he states that a second outer-shell electron can occupy a cell[18] only when all other cells contain at least one electron. The first of these statements requiring that electron shells be filled in a strictly sequential order was subsequently abandoned. Indeed, the precise order of shell and subshell filling has become an important question to assess the degree to which modern physics can explain the periodic system.[19]

But while, in the light of current knowledge, Langmuir's first statement appears to be incorrect, the second statement seems to anticipate an important aspect of modern quantum mechanical configurations, namely, the existence of Hund's rule. This rule states that when electrons are distributed among a number of orbitals with equal energies, they are placed in separate orbitals until the pairing of electrons into single orbitals becomes unavoidable.[20]

Langmuir's configurations appeared in pictorial form a couple of years later in a chemistry textbook written by Edward Washburn, as shown in figure 8.8.[21]

Contributions of Charles Bury

As mentioned above, Langmuir assumed that electron shells fill in a strictly sequential order. The first chemist to challenge this idea was Charles Bury, working at the University College of Wales in Aberystwyth.[22] In his article,[23] Bury states that the configurations he is proposing give a better explanation of the chemical properties of the elements than do those of Langmuir. He also notes that his own configurations dispense with the need to postulate cells as Langmuir does.

Contrary to Langmuir, Bury suggests that the number of electrons in the outer shell cannot be more than eight. Furthermore, he claims that an inner stable group of eight electrons can change into one containing 18 electrons, or that one of 18 can change into one of 32, in the course of the development of a transition series of elements (table 8.2). Bury supposes these transition elements to have more than one electronic structure, depending on their state of chemical combination. Although Bury's postulates do not lead to any disagreement with Langmuir's regarding the first few configurations, differences begin to appear in the first long period ranging from potassium to krypton.

Bury clearly states that electron shells do not fill sequentially when he writes, "Since eight is the maximum number of electrons in an outer layer K, Ca and Sc

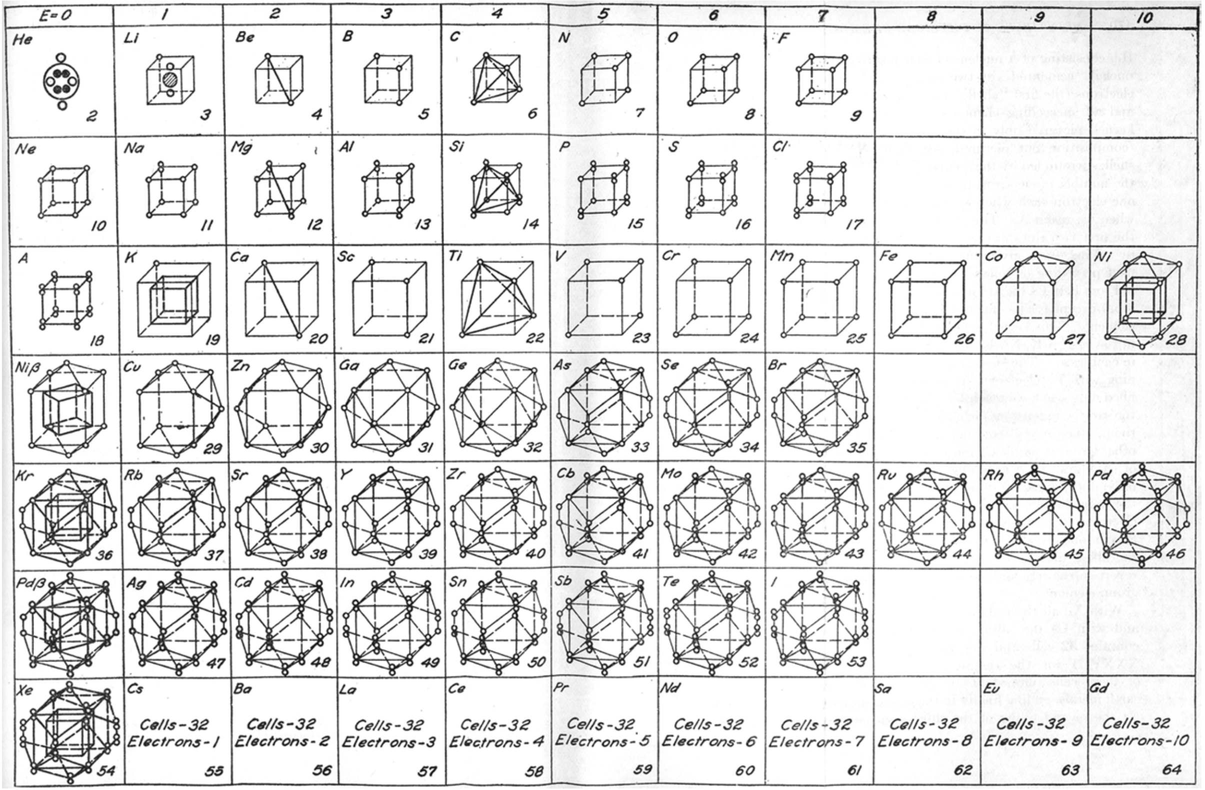


FIGURE 8.8 Langmuir's extended cubical atom models. From E.W. Washburn, *Introduction to the Principles of Physical Chemistry*, 2nd ed., McGraw-Hill, New York, 1921, p. 470.

TABLE 8.2
Bury's configurations for some first transition series atoms.

Ti	(2, 8, 8, 4)	(2, 8, 9, 3)	(2, 8, 10, 2)		
V	(2, 8, 8, 5)	(2, 8, 9, 4)	(2, 8, 10, 3)	(2, 8, 11, 2)	
Cr	(2, 8, 8, 6)	(2, 8, 11, 3)	(2, 8, 12, 2)		
Mn	(2, 8, 8, 7)	(2, 8, 9, 6)	(2, 8, 11, 4)	(2, 8, 12, 3)	(2, 8, 13, 2)
Fe	(2, 8, 10, 6)	(2, 8, 12, 4)	(2, 8, 13, 3)	(2, 8, 14, 2)	
Co	(2, 8, 13, 4)	(2, 8, 14, 3)	(2, 8, 15, 2)		
Ni	(2, 8, 14, 4)	(2, 8, 15, 3)	(2, 8, 16, 2)		
Cu	(2, 8, 17, 2)	(2, 8, 18, 1)			

C.R. Bury, Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 43, 1602-1609, 1921, table from p. 1603.

must form a fourth layer although their third is not complete. Their structures will be 2, 8, 8, 1; 2, 8, 8, 2, 2, 8, 8, 3." Furthermore, he infers that the elements from titanium to copper "form a transition series in which the incomplete group of eight in the third layer is changed to a saturated group of eighteen."[24] However, as mentioned above, Bury considers the elements from titanium to copper to possess more than one configuration, depending on what compounds they find themselves in, a suggestion that has not survived the test of time.[25]

The Case of Hafnium (Element 72)

The prediction and eventual confirmation that element 72 is not a rare earth element is widely regarded as a triumph for Bohr's theory of the periodic system. It is often argued that, while chemists believed that this element was a rare earth, Bohr drew on quantum theory to suggest otherwise. This is therefore presented as an early case of reduction of chemistry by quantum theory as distinct from the later quantum mechanics.

However, both parts of this commonly held view are partly mistaken. First, only a minority of chemists believed that hafnium should be a rare earth, and second, Bohr's prediction was not very conclusive and was based on a highly empirical theory of electron shells rather than on any deep theoretical principles. According to Bohr's theory, the rare earths are characterized by the building up of the N group or the fourth electron shell from the nucleus. On this view, the first rare earth is cerium with a fourth shell of the following configuration:[26]

$$\text{cerium}(58):(4_1)^6\,(4_2)^6\,(4_3)^6\,(4_4)^1$$

And the last rare earth is lutetium, with the following configuration:

$$\text{lutetium}(71):(4_1)^8\,(4_2)^8\,(4_3)^8\,(4_4)^8$$

The completion of the fourth shell represents the end of the rare earth series, and the next, as yet undiscovered, element is expected to be a transition metal and a homologue of zirconium, showing a valence of 4. The general approach used by Bohr in his assignment of electron shells is to ensure an overall agreement with the known periodic table. The form of the periodic table in fact guided Bohr to electronic configurations, as he sometimes admitted.

It emerges that the notion that element 72 was not a rare earth was the commonly held view among a number of chemists. Element 72, or at least the vacant space that it was supposed to fill, was often placed beyond the rare earth block in published periodic tables prior to Bohr's theory, for example, by Bury.[27] In fact, the prediction that hafnium is not a rare earth element can be obtained quite simply by counting and is by no means dependent on assuming the existence of electron shells. This can be illustrated as follows: It had been known for some time that the number of elements in each period follows a definite sequence given by 2, 8, 8, 18, 18, 32 (probably followed by 32), and so on. By adding the first six of these numbers, one arrives at the conclusion that the sixth period terminates with a noble gas of atomic number 86. It is a simple matter to work backward from this number to discover that element 72 should be a transition metal and a homologue of zirconium, which shows a valence of 4. This procedure depends on the plausible assumption that the third transition series should consist of 10 elements, as do the first and second transition series:

72,	73,	74,	75,	76,	77,	78,	79,	80,	81	82,	83,	84,	85,	86
...........10 transition metals...........										IV	V	VI	VII	VIII
1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	main group elements				

The only chemists who did indeed believe that element 72 was a rare earth were the few who specialized in obtaining these types of elements by painstaking separation of some mineral ores that were first found in Sweden. In 1879, Charles Marignac showed that the rare earth erbia could be separated into two rare earths, ytterbia and another element later called holmium (figure 8.9).[28] A year later, ytterbia was separated into two distinct elements named scandium and ytterbium. The next step was taken by Georges Urbain and Auer von Welsbach, who independently found that ytterbium itself could be separated into neo-ytterbium and lutetium. It was only natural that these workers should suspect the possibility of discovering further new elements by repeated separations of the same minerals.

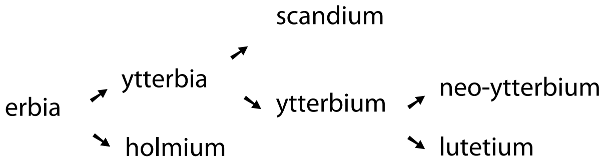


FIGURE 8.9 Sequence of discovery of some rare earth elements.

Urbain and von Welsbach both thought that ytterbium contained small amounts of a third rare earth that would possibly turn out to be element 72. Indeed, Urbain announced what he believed to be a positive spectroscopic identification of element 72 in 1911,[29] although this claim could not be confirmed by Moseley using his X-ray method. Urbain then abandoned his claim for 11 years, after which time he announced that together with Alexandre Dauvillier he had used a more accurate X-ray experiment and had detected two weak lines whose frequencies corresponded approximately to those expected for element 72 on the basis of Moseley's law. But this claim, too, turned out to be unfounded.[30]

Back to Bohr

As mentioned in chapter 7, when Bohr presented his method for ascribing electron shells, most physicists were puzzled by the manner in which he obtained his results. Letters to Bohr following the publication of his theory of the periodic system in *Nature* magazine[31] contain passages such Ernest Rutherford's: "Everybody is eager to know whether you can fix the rings of electrons by the correspondence principle or whether you have recourse to the chemical facts to do so."[32] And from Paul Ehrenfest: "I have read your article in Nature with eager interest. . . . Of course I am now even more interested to know how you saw it all in terms of correspondence."[33] Several years later, Hendrik Kramers wrote:

> It is interesting to recollect how many physicists abroad thought, at the time of the appearance of Bohr's theory of the periodic system, that it was extensively supported by unpublished calculations which dealt in detail with the structure of individual atoms, whereas the truth was, in fact, that Bohr had created and elaborated with a divine glance a synthesis between results of a spectroscopical nature and of a chemical nature.[34]

This remark seems to be particularly true regarding element 72, for which Bohr never produced any mathematical justification or any other form of argument resting specifically on quantum theory. Bohr's predictions regarding the electronic arrangements of the rare earths and that of hafnium were as follows.

First of all there are vague arguments based on "harmonic interaction," correspondence, and symmetry, such as the following:

> Even though it has not yet been possible to follow the development of the group [rare earths] step by step, we can even here give some theoretical evidence in favour of the occurrence of a symmetrical configuration of exactly this number of electrons. I shall simply mention that it is not possible without coincidence of the planes of the orbits to arrive at an interaction between four sub-groups of six electrons each in a configuration of simple trigonal symmetry, which is equally simple as that shown by these sub-groups. These difficulties make it probable that

> a harmonic interaction can be attained precisely by four groups containing eight electrons the orbital configurations of which exhibit axial symmetry.[35]

In a somewhat less obscure fashion, Bohr uses the counting argument mentioned above in order to arrive at the conclusion that element 72 should not be a rare earth:

> As in the case of the transformation and completion of the 3-quanta orbits in the fourth period and the partial completion of the 4-quanta orbits in the fifth period, we may immediately deduce from the length of the sixth period the number of electrons, namely 32, which are finally contained in the 4-quanta group of orbits. Analogous to what applied to the group of 3-quanta orbits it is probable that, when the group is completed, it will contain eight electrons in each of the four subgroups.[36]

According to Bohr, the element that represents the completion of the four-quanta groups and therefore marks the end of the rare earths is lutetium, with the following grouping of four-quanta electrons:

$$\text{lutetium}(71)\text{:}\ (4_1)^8\ \ (4_2)^8\ \ (4_3)^8\ \ (4_4)^8$$

Bohr writes:

> This element therefore ought to be the last in the sequence of consecutive elements with similar properties in the first half of the sixth period, and at the place 72 an element must be expected which in its chemical and physical properties is homologous with zirconium and thorium.[37]

He then adds: "This which is already indicated on Julius Thomsen's old table, has also been pointed out by Bury."[38]

In his Göttingen lectures on the periodic table, Bohr alluded to a calculation concerning the rare earth configurations. But this form of calculation was never produced by Bohr, nor has anything of the sort ever been found in the Bohr archives. Bohr also expressed a certain amount of doubt over his prediction that hafnium would not be a rare earth. Having explained the filling of the four-quanta groups as described above, he says: "However the reasons for indicating this arrangement are still weaker than in the case of the 3-quantic group and the preliminary closure of the 4-quantic group in silver."[39]

When Urbain and Dauvillier claimed to have discovered element 72 and that it was a rare earth, Bohr's initial response was to doubt his own prediction that it lay beyond the rare earths. This wavering was expressed in letters to colleagues as well as in the appendix of a book on atomic constitution.[40] He wrote to James Franck:

> The only thing I know for sure about my lectures in Göttingen is that several of the results communicated are already wrong. A first point is the constitution of element 72, which, as shown by Urbain and Dauvillier, contrary to expectations has turned out to be a rare earth element after all.[41]

And to Dirk Coster: "The question is apparently rather clear but one must of course always be prepared for complications. These may arise from the circumstance that we have to do with a simultaneous development of two inner electron rings."[42]

Bohr soon returned to his original claim about element 72. In doing so, he provided further examples of his essentially chemical arguments for his views on the missing element. In referring to the claim by Urbain and Dauvillier, Bohr points out that if element 72 is a rare earth, it should have a valence of 3 in common with other members of this group. Moreover, Bohr mentions that element 73, tantalum, is known to have a valence of 5: "This would mean an exception to the otherwise general rule, that the valency never increases by more than one unit when passing from one element to the next in the periodic table."[43]

Meanwhile, in response to the claims of Urbain and Dauvillier, which they believed to be unfounded, György von Hevesy and Coster, working at Bohr's institute in Copenhagen, began a search for element 72 in the ores of zirconium. Even their first attempt proved to be unexpectedly successful. After some further concentration of the new element, they obtained six clear X-ray lines whose frequencies were in very good agreement with Moseley's law applied to element 72.[44] The new element was named hafnium after *Hafnia*, Latin for Copenhagen, where the element had been discovered. The commonly cited story that Bohr instructed his colleagues to look for the new element in the ores of zirconium, where they discovered hafnium, is simply untrue. The suggestion to search for the new element within zirconium ores was made by a chemist, Fritz Paneth, based on purely chemical arguments.

No doubt the controversy over Urbain's claim and Bohr's theory stimulated this eventual true discovery of element 72, but in view of all the factors described above, it can still be doubted whether this development represents a successful chemical prediction on the basis of quantum theory. Had Bohr's theory been correct in making a prediction that had been contrary to the beliefs of the chemists of the day, this would have made Bohr's triumph all the greater, but this was not the case.

It might be more accurate to say that the view held by most chemists that hafnium would not be a rare earth was rationalized by Bohr's quantum theory of periodicity, which was partly empirical in origin. In addition, as noted above, Bury had already obtained the same correct prediction that hafnium was a transition metal, and not a rare earth, on the basis of purely chemical arguments.

John David Main Smith

John David Main Smith is another chemist who succeeded in producing more detailed electronic configurations and a more accurate explanation of the periodic system than did Bohr, but without receiving much credit at the time or in subsequent accounts of the development of the periodic system.[45]

TABLE 8.3
Bohr's subgroups consisting of equal subdivisions of electrons.

Quantum number	1	2	3	4
Number of electrons	2	8	18	32
Subgroups	1_2	$2_1, 2_2$	$3_1, 3_2, 3_3$	$4_2, 4_2, 4_2, 4_2$

N.Bohr, *Theory of Spectra and Atomic Constitution*, Cambridge University Press, Cambridge, UK, 1924, table based on p. 113.

In March 1924, Main Smith, at Birmingham University in England, published an article in the somewhat obscure journal *Chemistry and Industry*, in which he corrected an important feature in Bohr's electronic configurations, discussed in chapter 7.[46] Bohr's scheme of 1923 assumed that all subgroups of electrons were equally populated when full. For example, Bohr assumed that the second shell consisted of a total of eight electrons distributed equally into two subgroups, each containing four electrons (table 8.3). Main Smith challenged this notion on the basis of chemical, as well as X-ray diffraction, evidence.

Let us pause to consider the chemical arguments, especially in view of the general theme of the present book. In his 1924 book *Chemistry and Atomic Structure*, Main Smith begins a chapter titled "Atomic Structure and the Chemical Properties of Elements" with the following remark, which may seem obvious to chemists but perhaps not to physicists:

> Bohr's theory of atomic structure is strictly a theory relating to single atoms, neutral or ionised, far removed from the influence of other atoms. The fact that it is an interpretation of the periodic classification of the elements, largely based on the properties of atoms in combination, indicates that it must be valid for atoms in combination, at least so far as the broad outlines of the theory are concerned.[47]

He then proceeds to mount a sustained critique of the electronic configurations as assigned by Bohr on the basis that they do not take into account the chemical behavior of many of the elements. Main Smith points out that the elements of group III of the periodic table commonly display two distinct valences, a fact that cannot be explained from Bohr's configurations. He points out that the elements in group IV, and to some extent those of groups V, VI, and VII, commonly show two different valences. Main Smith remarked:

> This may be interpreted as evidence that all elements containing more than two valency electrons have two electrons, which, further interpreted in terms of orbits, indicates that that two electrons in the outer structure of atoms are in quantum orbits the energies of which are different from that of other outer electrons.[48]

From the point of view of our current knowledge, Main Smith had discovered that every main shell begins with an orbital containing just two electrons. However, another conclusion that is apparently equally drawn from chemical facts has turned out to be incorrect in the light of contemporary knowledge of electronic configurations. Main Smith argued that all the elements of groups V, VI, and VII have a marked tendency to form compounds with a coordination number of four and that this suggests that valence electrons in excess of four are "equally feebly attached to atoms." He interpreted this behavior to mean that any valence electrons in excess of four are all in similar quantum orbits. In fact, it is the six electrons in excess of two that form another shell in the atoms of successive elements, or in modern terminology, the following six electrons enter into three equivalent p orbitals.

Be that as it may, Main Smith concludes that the subgroups, in the second main shell, for example, should contain two, two, and four electrons, respectively, starting with the subgroup closest to the nucleus (table 8.3). He also states categorically that "[t]his evidence shows conclusively that Bohr's subgroup scheme, of two subgroups of four electrons for the two-quanta group, cannot be maintained."[49]

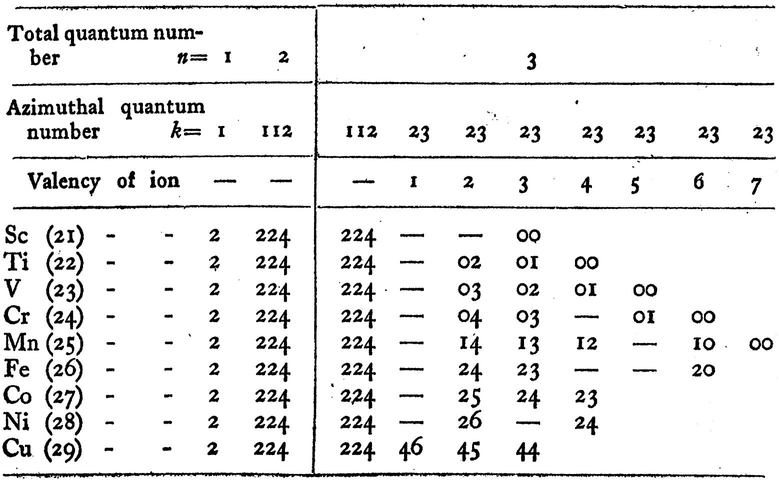
According to Bohr's set of configurations, the third shell consists of three subgroups, each of which contains six electrons. If this were indeed the case, Main Smith reasoned, we should expect to observe a single transition between levels 3_1 and 3_2, for example, in the X-ray spectrum of any element that possesses outer electrons in these levels. In fact, the X-ray evidence in the sodium atom spectrum, which is associated with the transition between these levels, is not a single line but the well-known sodium doublet. Main Smith concluded that there were additional levels between Bohr's levels 3_1 and 3_2. The subgroups of electrons for the elements in the second period according to Bohr and Main Smith, respectively, are compared in table 8.4. Main Smith proceeds to extend his list of configurations (figure 8.10), and with far greater detail than Bohr had published, for many of the elements up to gold ($Z = 79$).

Not surprisingly, these configurations have not withstood the test of time, since subgroups of four or eight electrons are not admitted in the modern scheme, which contains 2, 6, 10, or 14 in successive subshells of electrons.[50] However, these little known articles by Main Smith are of great historical interest because they show that some chemists not only understood Bohr's theory of periodicity but

TABLE 8.4
Subgroups of electrons in the second main shell for elements in the second period, according to Main Smith and Bohr.

	Bohr	*Main Smith*
Lithium	1	1
Beryllium	2	2
Boron	3	2, 1
Carbon	4	2, 2
Nitrogen	4, 1	2, 2, 1
Oxygen	4, 2	2, 2, 2
Fluorine	4, 3	2, 2, 3
Neon	4, 4	2, 2, 4

Compiled by the author.



Total quantum number $n=$	1	2	3							
Azimuthal quantum number $k=$	1	112	112	23	23	23	23	23	23	23
Valency of ion	—	—	—	1	2	3	4	5	6	7
Sc (21)	2	224	224	—	—	00				
Ti (22)	2	224	224	—	02	01	00			
V (23)	2	224	224	—	03	02	01	00		
Cr (24)	2	224	224	—	04	03	—	01	00	
Mn (25)	2	224	224	—	14	13	12	—	10	00
Fe (26)	2	224	224	—	24	23	—	—	20	
Co (27)	2	224	224	—	25	24	23			
Ni (28)	2	224	224	—	26	—	24			
Cu (29)	2	224	224	46	45	44				

FIGURE 8.10 Configurations of some transition elements, extracted from more complete tables of configurations. J.D. Main Smith, *Chemistry and Atomic Structure*, Ernest Benn Ltd., London, 1924, p. 196.

were prepared to grapple with its details, including the physical evidence such as that obtained from X-ray spectroscopy. Moreover, several chemists were able to deduce more comprehensive explanations of the periodic system in terms of electronic configurations, as in the case of Main Smith.

As mentioned in chapter 7, the next major step after Bohr's two-quantum-number account was given by Stoner. It emerges that Stoner's scheme is almost identical to the one by Main Smith just described. The two scientists arrived at their respective versions independently, although Main Smith was the first to publish. Both of them drew upon a detailed analysis of X-ray spectra to arrive at their electron subgroups.

Main Smith correctly considered that his contributions had not been properly acknowledged and wrote the following published letter to the editor of *Philosophical Magazine*:

> [A]ttention to the fact that the distribution of electrons in atoms characterized by the subgroupings 2; 2,2,4; 2,2,4,4,6; 2,2,4,4,6,6,8 did not originate with Mr. E. Stoner, as within recent months various papers published in your journal have suggested.[51]

It is gratifying to note that Stoner indeed conceded Main Smith's priority when, a couple of years later in a textbook of atomic physics, he wrote,

> I have since found that my distribution had already been proposed, primarily on the basis of chemical arguments by Main Smith. It is very satisfactory that two different lines of attack should have led to the same conclusions.[52]

This is a fitting conclusion to this chapter, which has demonstrated how chemistry was by no means eclipsed by the discoveries in atomic physics. The cases of Main

Smith and Bury, in particular, show that chemists not only were able to compete with the atomic physicists on their own terms but also arrived at more detailed configurations before the physicists could do so.

Conclusion

In a matter of a few years, several chemists, including Lewis, Langmuir, and Bury, had obtained detailed electronic configurations for all the known elements, including the more complicated transition elements. Bury had realized that the atoms of the transition elements do not fill their electron shells in sequential order and had predicted that element 72 would be a transition metal that would show chemical similarities with zirconium. All this work was achieved without any arguments based on theoretical physics or, more specifically, without using quantum theory. The chemists' configurations were obtained inductively on the basis of the chemical properties of the elements. This aspect of the history of the periodic system is seldom emphasized, with most accounts promoting the view that electronic configurations resulted entirely from the work of theoretical physicists such as Bohr. In truth, Bohr had also reached electronic configurations inductively, frequently drawing on chemical evidence, as the chemists themselves had done. Bohr's configurations were frequently less detailed in that he specified only those of the closed-shell atoms of the noble gases and did not cite those of the intervening series of elements in each period of the table.

The popular story according to which Bohr predicted the chemical nature of element 72, subsequently named hafnium, has been criticized and can no longer be sustained by anyone who examines the historical evidence surrounding this case.[53] Indeed, Bohr seems to have arrived at many configurations by appeal to chemical as well as other experimental data that he then dressed up in quantum mechanical language through his characteristically obscure style of writing.

It is also quite possible that Bohr could have relied quite heavily on the work of Bury, who had predicted that element 72 would be a transition element. Bury's priority in this matter is even conceded by Bohr himself in his articles, although he does not seem to attach much significance to Bury's prediction, presumably because it is not couched in terms of the quantum theory. In addition, whereas Bohr initially gave configurations only for the noble gases, he appears to have begun listing those of the intervening elements only after the appearance of Bury's detailed versions published in 1921.

The case for Bury's priority over Bohr in these matters has been valiantly argued by one of Bury's former students, Mansel Davies, who published a number of articles to this effect.[54] This claim has been taken up and amplified by Keith Laidler, the distinguished chemical kineticist and historian.[55] While it may be that Bury's work has been highly neglected, perhaps a more conservative conclusion may be more appropriate. The neglect of Bury's work may not be due to any duplicity by Bohr, or his supporters, but rather because Bury gave chemical arguments for his own assignment of configurations, whereas the prevailing reductionist climate implied that quantum mechanics inevitably provides a more fundamental explanation for the periodic system.[56] A fuller discussion of this issue is given in chapter 9, which includes an analysis of the reduction of the periodic system using quantum mechanics.

And finally, the chemist Main Smith, drawing on the same X-ray data as the atomic physicist Stoner, as well as chemical evidence, was able to arrive at the conclusion that the number of electrons in each subgroup was twice the value of the inner quantum number. He thus obtained the same electron subgrouping several months before Stoner, whose discovery of the same concept is far better acknowledged by historians of science.

Notes

1. The following is a quotation from Lewis:

> I went from the Middle-west to study at Harvard, believing that at the time it represented the highest scientific ideals. But now I very much doubt whether either the physics or the chemistry department at that time furnished real incentive to research.…A few years later [1902] I had very much the same ideas of atomic and molecular structure as I now hold, and I had a much greater desire to expound them, but I could not find a soul sufficiently interested to hear the theory. There was a great deal of research being done at the university, but as I see it now the spirit of research was dead.

G.N. Lewis to R. Millikan, October 28, 1919, Lewis Archive, University of California, Berkeley, as cited in R.E. Kohler, The Origin of G.N. Lewis's Theory of the Shared Pair Bond, *Historical Studies in the Physical Sciences*, 3, 343–376, 1971, which is the definitive study on Lewis.

2. In addition, Thomson had not been able to deduce the correct number of electrons even in atoms as simple as oxygen.

3. The notion of a shared pair of electrons survives, to some extent, in the quantum mechanical treatment of the atom. In the current model, a bond consists of two antiparallel electrons within the same molecular orbital.

4. G.N. Lewis, The Atom and the Molecule, *Journal of the American Chemical Society*, 38, 762–785, 1916.

5. See a chapter on Abegg in E.R. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016, 63–78.

6. The term "amphoteric" is now taken to mean an oxide or hydroxide that can dissolve in acids to give salts and can also dissolve in alkalis to give metallates; i.e., it can show both basic and acidic properties. Examples include the oxides and hydroxides of boron and aluminum.

7. A. Stranges, *Electrons and Valence: Development of the Theory 1900–1925*, Texas A&M University Press, College Station, 1982, quoted from p. 204.

8. G.N. Lewis, The Atom and the Molecule, *Journal of the American Chemical Society*, 38, 762–785, 1916, quoted from p. 768.

9. The notion of magnetic properties in electrons did not originate with Lewis but had been previously discussed by Alfred Parsons and William Ramsay. See A. Parsons, A Magneton

Theory of the Atom, *Smithsonian Miscellaneous Publications*, 65, 1–80, 1915; W. Ramsay, A Hypothesis of Molecular Configuration, *Proceedings of the Royal Society A.*, 92, 451–462, 1916.

10. See, e.g., J. Servos, *Physical Chemistry from Ostwald to Pauling*, Princeton University Press, Princeton, NJ, 1990.

11. This forms the basis of numerous examples used to this day to torment the lives of chemistry students attempting to write Lewis structures for any given number of molecules.

12. As discussed in chapter 6, Moseley provided a method of determining the nuclear charge and consequently the number of electrons in any atom.

13. This is also true of the octet rule, which Lewis himself was not so keen on.

14. I. Langmuir, The Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 43, 1602–1609, 1921, quoted from p. 869.

15. Kossel was a physicist who published a theory of ionic bonding in 1916. W. Kossel, Uber Molekulbildung als Frage des Atombaus, *Annalen Der Physik,* 49, 229–362, 1916.

16. Niton is now called radon.

17. The inclusion of Niβ and other elements followed by Greek letters is somewhat mysterious and not explained in Langmuir's text. It would appear that he is attempting to avoid any gaps in the periodic table, although gaps do occur in later parts of his table.

18. A cell can contain up to two electrons and, as such, can be thought of as analogous to the modern concept of an orbital, which can also accommodate a maximum of two electrons.

19. In the modern version of electronic configurations, there are several places in the periodic table where a new shell begins to fill even though the previous shell is not yet completely full. The attempts to explain such features are resumed in chapter 9.

20. This analogy depends on identifying one of Langmuir's cells, which can hold two electrons, with the modern notion of an atomic orbital.

21. This time, only some of the closed-shell atoms appear twice in the table, namely, nickel and palladium, but not the noble gases.

22. Saul Dushman, one of Langmuir's colleagues at the General Electric Company in Schenectady, New York, had been the first to publish ideas on incomplete shells in transition metal atoms at the suggestion of Langmuir himself. S. Dushman, The Structure of the Atom, *General Electric Review*, 20, 186–196, 397–411, 1917.

23. C.R. Bury, Langmuir's Theory on the Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 43, 1602–1609, 1921.

24. Modern configurations differ slightly in that the transition metals are supposed to begin one element earlier, namely, at scandium, which is the first element where the filling of the third shell is resumed.

25. See a chapter on Bury in E.R. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016, 79–102.

26. Superscripts denote the number of electrons in each quantum level.

27. C.R. Bury, Langmuir's Theory on the Arrangement of Electrons in Atoms and Molecules, *Journal of the American Chemical Society*, 43, 1602–1609, 1921.

28. M.E. Weeks, *Discovery of the Elements*, 6th ed., Easton, PA, 1956.

29. G. Urbain, Sur un Nouvel Élément qui Accompagne le lutécium et le scandium dans les terres de la gadolinite: le celtium, *Comptes Rendus*, 152, 141–143, 1911.

30. A chapter on the discovery of element-72, including some earlier claims and debates, appears in E.R. Scerri, *A Tale of Seven Elements*, Oxford University Press, New York, 2013, 84–99.

31. N. Bohr, Atomic Structure, *Nature*, 107, 104–107, 1921.

32. E. Rutherford, letter to N. Bohr, September 26, 1921, in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 4, North-Holland Publishing Company, Amsterdam, 1981.

33. P. Ehrenfest, letter to N. Bohr, September 27, 1921, in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 4, North-Holland Publishing Company, Amsterdam, 1981.

34. H. Kramers, quoted in H. Kragh, The Theory of the Periodic System, in A.P. French, P.J. Kennedy (eds.), *Niels Bohr, A Centenary Volume*, Harvard University Press, Cambridge, MA, 1985, 50–67, quoted from p. 60.

35. N. Bohr, *The Theory of Spectra and Atomic Constitution*, 2nd ed., Cambridge University Press, Cambridge, 1924, p. 110.

36. Ibid., p. 114.

37. Ibid.

38. Ibid.

39. Lecture Six of Seven Lectures on the Theory of Atomic Structure (Göttingen, 1922), in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 4, North-Holland Publishing Company, Amsterdam, 1981, 397–406, quoted from p. 404.

40. N. Bohr, *The Theory of Spectra and Atomic Constitution*, 2nd ed., Cambridge University Press, Cambridge, 1924, appendix.

41. N. Bohr, letter to J. Franck, July 15, 1922, in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 4, North-Holland Publishing Company, Amsterdam, 1981, p. 675, translation on p. 676.

42. N. Bohr, letter to D. Coster, July 3, 1922, in *Collected Papers of Niels Bohr*, edited by J. Rud Nielsen, vol. 4, North-Holland Publishing Company, Amsterdam, 1981, as quoted in H. Kragh, Niels Bohr's Second Atomic Theory, *Historical Studies in the Physical Sciences*, 10, 123–186, 1979.

43. N. Bohr, *The Theory of Spectra and Atomic Constitution*, 2nd ed., Cambridge University Press, Cambridge, 1924, quoted from p. 114.

44. D. Coster, G. von Hevesy, On the Missing Element of Atomic Number 72, *Nature*, 111, 79, 1923.

45. A chapter on the work of Main Smith appears in E.R. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016, 117–148.

46. J.D. Main Smith, Atomic Structure, *Chemistry and Industry*, 43, 323–325, 1924. Main Smith had previously published an article citing numerous criticisms of Bohr's electronic configurations but without suggesting any alternatives himself. J.D. Main Smith, The Bohr Atom, *Chemistry and Industry*, 42, 1073–1078, 1923.

47. J.D. Main Smith, *Chemistry and Atomic Structure*, Ernest Benn Ltd., London, 1924, p. 189.

48. Ibid., p. 190.

49. Ibid., p. 192.

50. In the sense of s, p, d, and f subshells, respectively.

51. J.D. Main Smith, The Distribution of Electrons in Atoms [letter dated September 8], *Philosophical Magazine*, 50(6), 878–879, 1925, quoted from p. 878.

52. E. Stoner, *Magnetism and Atomic Structure*, Methuen & Co., London, 1925, p. 1296 footnote.

53. H. Kragh, Niels Bohr's Second Atomic Theory, *Historical Studies in the Physical Sciences*, 10, 123–186, 1979; H. Kragh, Chemical Aspects of Bohr's 1913 Theory, *Journal of Chemical Education*, 54, 208–210, 1977.

54. Mansel Davies, Charles Rugeley Bury and his Contributions to Physical Chemistry, *Archives for the History of the Exact Sciences*, 36, 75–90, 1986.

55. K.J. Laidler, *The World of Physical Chemistry*, Oxford University Press, New York, 1993.

56. The question of the reduction of chemistry to quantum mechanics has been a central issue in the renewed interest in philosophical aspects of chemistry. L. McIntyre, The Emergence of the Philosophy of Chemistry, *Foundations of Chemistry*, 1, 57–63, 1999; J. van Brakel, On the Neglect of the Philosophy of Chemistry, *Foundations of Chemistry*, 1, 111–174, 1999; E.R. Scerri, L. McIntyre, The Case for the Philosophy of Chemistry, *Synthese,* 111, 305–324, 1997.

CHAPTER 9

QUANTUM MECHANICS AND THE PERIODIC TABLE

In chapter 7, the influence of the old quantum theory on the periodic system was considered. Although the development of this theory provided a way of reexpressing the periodic table in terms of the number of outer-shell electrons, it did not yield anything essentially new to the understanding of chemistry. Indeed, in several cases, chemists such as Irving Langmuir, J.D. Main Smith, and Charles Bury were able to go further than physicists in assigning electronic configurations, as described in chapter 8, because they were more familiar with the chemical properties of individual elements. Moreover, despite the rhetoric in favor of quantum mechanics that was propagated by Niels Bohr and others, the discovery that hafnium was a transition metal and not a rare earth was not made deductively from the quantum theory.[1] It was essentially a chemical fact that was accommodated in terms of the quantum mechanical understanding of the periodic table.

The old quantum theory was quantitatively impotent in the context of the periodic table since it was not possible to even set up the necessary equations to begin to obtain solutions for the atoms with more than one electron. An explanation could be given for the periodic table in terms of numbers of electrons in the outer shells of atoms, but generally only after the fact. But when it came to trying to predict quantitative aspects of atoms, such as the ground-state energy of the helium atom, the old quantum theory was quite hopeless. As one physicist stated, "We should not be surprised…even the astronomers have not yet satisfactorily solved the three-body problem in spite of efforts over the centuries."[2] A succession of the best minds in physics, including Hendrik Kramers, Werner Heisenberg, and Arnold Sommerfeld, made strenuous attempts to calculate the spectrum of helium but to no avail.

It was only following the introduction of the Pauli exclusion principle and the development of the new quantum mechanics that Heisenberg succeeded where everyone else had failed. In fact, Heisenberg performed the calculation using both his own matrix mechanics and Erwin Schrödinger's wave mechanics as discussed below. In terms of wave mechanics, Heisenberg interpreted his result as showing the need for the overlap between the wavefunctions of the two electrons in helium. This overlap, which he called an "exchange term," was due entirely to the indistinguishability of the two electrons. This meant that the terms in the equation had to be written in two ways, the second of which involved the exchange of labels to account for the fact that both electrons are identical. Such exchange terms[3] are highly nonclassical and follow from Wolfgang Pauli's discovery of the exclusion principle.

This discovery was to be the beginning of the use of exchange terms in the quantum mechanics of atoms and molecules. It became the key factor that shortly afterward allowed Walter Heitler and Fritz London to obtain the first successful quantum mechanical calculation of the covalent bond in the simplest case of a diatomic hydrogen molecule. Exchange terms would also pave the way for the notion of quantum mechanical resonance and the development of the quantum mechanical theories of bonding by Linus Pauling and many others.[4]

Perhaps the key advance that quantum mechanics provided, compared with the old quantum theory, was that the quantization itself seemed to arise in a more natural manner. In the old quantum theory, Bohr had been forced to postulate that the angular momentum of electrons was quantized, while the advent of quantum mechanics showed that this condition was provided by the theory itself and did not have to be introduced by fiat. For example, in Schrödinger's version of quantum mechanics, the differential equation is written, and certain boundary conditions are applied, with the result that quantization emerges automatically.

A conceptual grasp for how the application of boundary conditions to waves leads naturally to quantization can be obtained from the following analogy. Suppose that a string is tied at both ends and is made to vibrate. It turns out that the string can adopt one of many possible standing wave patterns where certain points along the string remain stationary. As shown in figure 9.1, the string can vibrate either as a whole or with a number of so-called nodes, each of which represents a stationary point along the string.

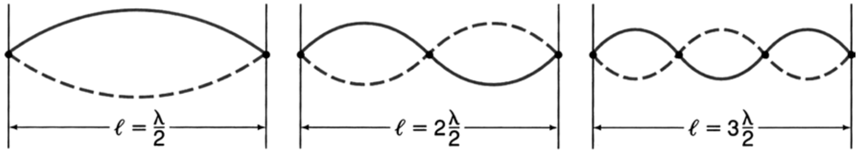


FIGURE 9.1 The imposition of boundary conditions produces quantization in a vibrating wave. From R. Chang, *Physical Chemistry for the Chemical and Biological Sciences*, University Science Books, Sausalito, CA, 2000, p. 576. By permission from the publisher.

In other words, the mere presence of waves that are bound at both ends immediately implies quantization of the form described above. The string can vibrate only in a number of well-defined ways that have 0, 1, 2, 3, and so on, nodes. No other intermediate vibrational nodes can exist, and this is the essence of quantization associated with any kind of standing wave phenomenon.

From Bohr's Old Quantum Theory to Quantum Mechanics

What Bohr had been doing in his explanations of the periodic table was not deducing electronic configurations from first principles, as he led his readers to believe; rather, he was essentially working backward from chemical and spectroscopic facts and showing that these facts were consistent with a quantum theoretical description.

But the old quantum theory was only the beginning of quantum mechanics, which is the most powerful physical theory that has ever been devised. The transition between the old quantum theory and the new quantum mechanics is examined in this chapter, as is the impact that the updated theory had on attempts to understand the periodic table. As I argue here, the effect has been considerable, but surprisingly still incomplete, from the fundamental point of view of trying to provide a deeper explanation of the periodic system. Nevertheless, many forms of more accurate calculations can now be carried out in quantum chemistry than were even dreamt of at the time of the old quantum theory.

Although it is not my intention to give a history of the transition between Bohr's old quantum theory and the later quantum mechanics, it is necessary to sketch some of the steps that were taken. In fact, one of the connecting steps between the old and the new versions of quantum theory is mentioned in chapter 7, because it provided the culminating step in the explanation of the periodic system as it is still generally understood. This was the introduction by Pauli of the fourth quantum number and his subsequent discovery of the Pauli exclusion principle, which dictates that no two electrons in an atom can possess the same four quantum numbers. What follows from this assumption is an elegant explanation of the possible lengths of any period, but only provided that one is willing to admit some experimental information into the explanation.

As noted in chapter 7, an explanation can be given for the maximum possible number of electrons in any shell around the nucleus. The formula $2n^2$, which had been recognized for some time as summarizing the number of elements in any particular period, is thus given an apparent theoretical underpinning. But there is one aspect, the order of shell filling, that has not yet been deduced from first principles. This issue cannot be avoided if one is to really ask whether quantum mechanics explains the periodic system in a fundamental manner.

The Advent of Quantum Mechanics

The old quantum theory reached a crisis point around 1924–1925, at which time it was realized that a more radical theory would be needed in order to settle a number of outstanding problems in physics. One of these problems of particular importance to the story of the periodic table was the attempt to calculate the properties of helium, the second atom in the periodic table following hydrogen. Whereas the old quantum theory provided a means of obtaining an exact solution to the calculation of the energy of the hydrogen atom, the move to considering helium appeared to cause insurmountable problems. It was not that the solution of this problem was just difficult in the old quantum theory. It was not even possible to formulate the necessary equations adequately.

Only following the advent of quantum mechanics, as distinct from the old quantum theory, was there a possibility of calculating the energy of helium, and even then only approximately. Developments initially occurred along two distinct lines. First of all, Heisenberg, a very young German, developed an approach that eventually became known as matrix mechanics. Heisenberg's original motivation appears to have been the complete abandonment of unobservable features of the world, such as atomic orbits.[5] This followed the realization that atomic orbits were quite different from the orbits of planets and other macroscopic objects. They were eventually renamed "orbitals" instead of orbits, a name intended to mean a form of motion without a definite trajectory. Unfortunately, the change in terminology is too subtle, with the result that many chemists, in particular, still seem to maintain some form of pathlike visualization.[6]

Heisenberg intended to build a theory centered on observable quantities such as spectral frequencies. The theory that he developed was highly counterintuitive and required physicists to invest much time and effort in learning a new branch of mathematics dealing with the manipulation of matrices. In addition, the attempt to reject unobservable quantities that Heisenberg had hoped for was not realized.

At about the same time, Schrödinger developed what came to be known as wave mechanics. Already in 1924, the French physicist Prince Louis De Broglie had suggested an analogy to Albert Einstein's earlier discovery that light waves have a particulate nature as well as their expected wave nature. De Broglie made the association run in the opposite sense. Why not suppose that particles such as electrons could likewise display wavelike properties? The test for this idea would be to demonstrate experimentally that electrons produce diffraction and interference effects just like classical waves, such as waves on the surface of water.[7]

Two physicists, Clinton Davisson and Lester Germer, successfully carried out just such an experiment in 1927, thus giving experimental support to De Broglie's proposal.[8] With this discovery, theorists such as Schrödinger received the impetus to further pursue the mathematical analogies between classical waves and electron waves.[9] Whereas Heisenberg's approach was mathematically abstract, that of

Schrödinger was more familiar to chemists because it dealt principally with wave motion. Unlike Heisenberg, Schrödinger had not originally tried to break with realistic notions of the microscopic world and, in fact, had hoped that his method would retain strong connections with classical physics and physical visualization.

As it turned out, neither Heisenberg's nor Schrödinger's hopes materialized fully. The quantum mechanics that emerged after a few years of intense debate was not based solely on observable properties, nor was it possible to retain a realistic view of matter waves as Schrödinger had originally hoped. Moreover, the two forms of quantum mechanics were shown to be equivalent.[10]

The new theory became centered on the wavefunction for an atom or a molecule. This wavefunction could be expressed with a number of terms called "atomic orbitals." As mentioned above, the name was derived from atomic orbits of the old quantum theory but without any intended connection with a definite trajectory for the electron. Such orbitals inhabit a multidimensional Hilbert space in quantum mechanics, thus further denying their visualizability in familiar three-dimensional space. Moreover, wavefunctions and their component building blocks consisting of such orbitals are themselves complex mathematical functions in the sense that they contain factors involving the square root of –1.

What is observable in the case of wavefunctions, as it emerged a little later, is the square of the wavefunction,[11] which is called the electron density.[12] In addition, even the square of the wavefunction cannot be obtained for a single electron at a specific point. The interpretation of quantum mechanics calls for a statistical view in which one can know only the probability of an electron residing in a certain region of space.

Hartree-Fock Method

When it comes to calculating the properties of atoms, the new quantum mechanics provides a way in which the problem can be attacked by means of approximation methods.[13] The basis of the most widely used approximation for solving quantum mechanical equations for atoms is called the Hartree-Fock method after Douglas Hartree (figure 9.2) and Vladimir Fock, an English and a Russian physicist, respectively.[14]

The main assumption made in the Hartree-Fock model is that any given electron moves in a field resulting from the attraction of the nucleus added to the field that results from the sum of all the remaining electrons. This approach avoids dealing directly with individual electron–electron repulsion terms, and instead, one recovers a situation not altogether unlike that of the hydrogen atom in which one electron is moving in a spherically symmetrical field. In the many-electron case, the field consists of those of the nucleus and of all the other electrons lumped together. The only difference is that instead of one equation for one electron, there

FIGURE 9.2
Douglas Hartree. Photo and permission from Emilio Segrè Collection.

are now as many equations as there are electrons in the atom. In addition, the solution for each electron must be consistent with those for all the other electrons, thus requiring a self-consistent iteration procedure that is typically carried out on a computer.

But let us return to the question of the explanation of periodicity, which opened this chapter. The Pauli exclusion principle and the use of four quantum numbers only provide a deductive explanation of the total number of electrons that any electron shell can hold. The correspondence of these values with the number of elements that occur in any particular period is something of a coincidence. The lengths of successive periods have not yet been strictly deduced from the theory.[15] However, most chemistry and physics textbook authors do not emphasize or even mention this point. As a result, they imply that quantum mechanics does indeed provide a perfectly satisfactory deductive explanation of the periodic system. This, in turn, fuels the general impression that chemistry is fully explained by quantum physics and has a negative effect on chemical education. Instead of starting from chemical facts, and the properties of the elements, the modern tendency is to expose students to the rules for electronic configurations in the belief that the chemistry will somehow follow.[16] Nevertheless, the number of electrons contained in any shell, as opposed to the lengths of periods, does emerge directly from the rules for combining the four quantum numbers. This part of the explanation for periodicity is completely satisfactory, as shown in the next section.

Writing Electronic Configurations for Atoms

The assignment of electronic configurations to the atoms in the periodic table proceeds according to three principles:

1. The *aufbau* principle (*aufbauprinzip* in chapter 7): Orbitals are occupied in order of increasing values of $n + \ell$. For example, the 4s orbital for which $n + \ell = 4$ is filled before the 3d orbital for which $n + \ell = 5$. This rule is often accompanied by a diagram like the one shown in figure 9.3, which represents the Madelung or $n + \ell$ rule.
2. The Hund principle: When electrons fill orbitals of equal energies, they occupy as many different orbitals as possible.
3. The Pauli exclusion principle: Only two electrons can occupy a single orbital, and if they do so, they must orient their spin angular momenta in opposite directions.[17]

Several points need to be made about these principles. The first principle does not, in fact, refer to the ordering of energies of atomic orbitals. What it really refers to is the order of filling of the various orbitals. These are related but separate issues. But there is more involved in the occupation of orbitals than their individual energies, as discussed further below. The $n + \ell$ rule has not yet been derived from the principles of quantum mechanics. The leading quantum chemist, Per-Olov Löwdin, has described this failure as one of the outstanding problems in quantum mechanics.[18]

It emerges that all three of these principles are essentially empirical, and none of them has been strictly derived from the principles of quantum mechanics.[19] Pauli's principle, for example, takes the form of an additional postulate to the main postulates of quantum mechanics. Despite strenuous efforts on the part of many physicists, including Pauli himself, it has never been possible to derive the principle from the postulates of quantum mechanics and/or relativity theory.[20] So, rather

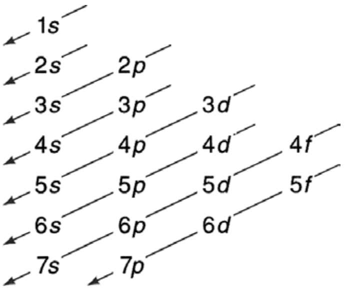


FIGURE 9.3
Madelung (or $n + \ell$ rule) for the order of filling of orbitals. From R. Chang, *Physical Chemistry for the Chemical and Biological Sciences*, University Science Books, Sausalito, CA, 2000, p. 601. By permission from the publisher.

than providing an explanation for electronic configurations, the three commonly used rules are really statements that summarize what is known to happen from experimental data on atomic spectra.

And now let us turn to the explanation for the number of electrons in each shell and its connection to the number of elements in each subsequent period of the periodic table. These facts are usually explained in terms of the relationship between the four quantum numbers, which can be assigned to any electron in a many-electron atom. The relationship between the first three quantum numbers is rigorously deduced from the Schrödinger equation for the hydrogen atom. The first quantum number, n, can adopt any integral value starting with 1.[21] The second quantum number, which is given the label ℓ, can have any of the following values related to the values of n:

$$\ell = n - 1, \ldots 0$$

In the case when $n = 3$, for example, ℓ can take the values 2, 1, or 0. The third quantum number, labeled m_ℓ, can adopt values related to those of the second quantum numbers:

$$m_\ell = -\ell, -(\ell - 1), \ldots 0 \ldots (\ell - 1), \ell$$

For example, if $\ell = 2$, the possible values of m_ℓ are –2, –1, 0, +1, and +2. Finally, the fourth quantum number, labeled m_s, can take only two possible values, either +1/2 or –1/2 units of spin angular momentum. There is therefore a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom.

As a result of this scheme, it is clear why the third shell, for example, can contain a total of 18 electrons. If the first quantum number, given by the shell number, is 3, there will be a total of $2 \times (3)^2$ or 18 electrons in the third shell.[22] The second quantum number, ℓ, can take values of 2, 1, or 0. Each of these values of ℓ will generate a number of possible values of m_ℓ, and each of these values will be multiplied by a factor of 2 since the fourth quantum number can adopt values of 1/2 or –1/2.

But the fact that the third shell can contain 18 electrons does not strictly explain why it is that some of the periods in the periodic system contain 18 places. It would be a rigorous explanation of this fact only if electron shells were filled in a strictly sequential manner. Although electron shells begin by filling in a sequential manner, this ceases to be the case starting with element 19, potassium. Since the configuration of element 18, argon, is

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6,$$

one might expect the configuration for element 19, potassium, would be

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1.$$

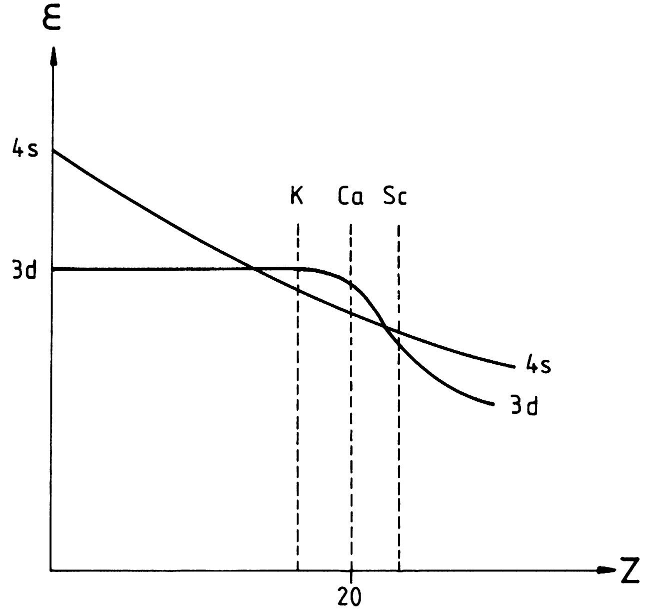


FIGURE 9.4 The relative ordering of the 3d and 4s energy levels. L.G. Vanquickenborne, K. Pierloot, D. Devoghel, *Journal of Chemical Education*, 71, 469–471, 1994, p. 469. By permission from the publisher.

This would be expected because up to this point the pattern has been one of adding the differentiating electron to the next available orbital at increasing distances from the nucleus. However, experimental evidence shows that the configuration of potassium should be denoted as

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

As many textbooks explain, this can result from the fact that the 4s orbital has a lower energy than the 3d orbital for the atoms of potassium and calcium (see figure 9.4).

In the case of element 20, calcium, the new electron also enters the 4s orbital. But in the case of element 21, scandium, the orbital energies have reversed so that the 3d orbital has a lower energy. Textbooks typically claim that since the 4s orbital is already full, the next electron necessarily begins to occupy the 3d orbital. This pattern is supposed to continue across the first transition series of elements, apart from the elements chromium and copper, where further anomalies occur (table 9.1).

TABLE 9.1
Electronic configurations for first transition metals.

Sc	$4s^23d^1$
Ti	$4s^23d^2$
V	$4s^23d^3$
Cr	$4s^13d^5$
Mn	$4s^23d^5$
Fe	$4s^23d^6$
Co	$4s^23d^7$
Ni	$4s^23d^8$
Cu	$4s^13d^{10}$
Zn	$4s^23d^{10}$

In fact, this explanation for the configuration of the scandium atom, and most other first transition elements, is inconsistent.[23] The argument that most textbooks present is incorrect since it should be possible to predict the configuration of an element from knowledge of the order of its own orbital energies. One should not have to consider the configuration of the previous element and assume that this configuration is somehow carried over intact on moving to the next element.

What seems to be a closely guarded secret is that the 4s orbital is not preferentially occupied in transition metals starting at scandium. Since the 3d orbitals have lower energy than 4s, starting at scandium they are the orbitals that are preferentially occupied.

The traditional account incorrectly claims that all transition elements show a preferential occupation for an s orbital, and yet that the s electrons are also the easiest to ionize. This situation may be represented by two diagrams, one for relative occupation and one for relative ionization of orbitals in the first transition series, as shown in figure 9.5.

The two diagrams are inconsistent. Either one or the other applies but not both at once, since the occupation of orbitals in energetic terms is the reverse of the process of successive ionization. In fact, it is the right-hand diagram that is the correct one.

The apparently blatant mistake of claiming that 4s orbitals are preferentially occupied in transition metal atoms has taken root in chemical education circles. This is presumably because the *aufbau* diagram gives the *overall* configuration correctly in all but about 20 cases. However, when one asks questions about the order of orbital occupation, this approach gives an incorrect prediction. Unfortunately, maintaining this way of teaching electronic configurations leads many instructors and textbooks to invent all kinds of contorted schemes to explain why, even

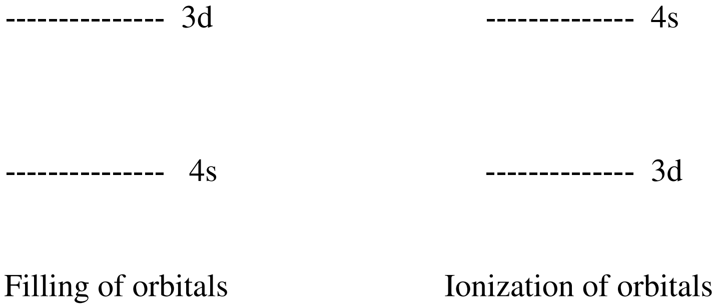


FIGURE 9.5 Ordering of orbital energies as implied by relative filling and relative ionization. The lower the level, the more stable the atom.

though the 4s orbital fills preferentially (which it does not in reality), it is also the 4s electron that is preferentially ionized to form an ion of Sc^+. These explanations are incorrect, since the 4s orbital actually fills last; consequently, it is perfectly natural that it should be the first orbital to lose an electron on forming a positive ion.

Examining the Evidence

The evidence that refutes the view that what I term the "sloppy version" of the *aufbau* principle comes from experimental spectral evidence from the various ions of any transition metal atoms.[24] Using scandium as an example, we have:

Sc^{3+} $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^0, 4s^0$
Sc^{2+} $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^0$
Sc^{1+} $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^1$
Sc $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$

On moving from the Sc^{3+} ion to that of Sc^{2+}, it is clear that the additional electron enters a 3d orbital and not a 4s orbital as the *aufbau* diagram implies (figure 9.3). Similarly on moving from this ion to the Sc^{1+} ion, the additional electron enters a 4s orbital as it also does in arriving at neutral scandium atom or Sc. Similar patterns and sequences are observed for the subsequent atoms in the periodic table, including titanium, vanadium, chromium,[25] manganese, and so on.

Returning to scandium, and now following the correct version of the *aufbau* principle in which energy levels are filled with electrons in order of decreasing stability, we note that the 3d orbitals should have a lower energy than 4s. Therefore, when predicting the way that the electrons fill in scandium, we might suppose that the final three electrons after the core argon configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ would all enter into some 3d orbitals to give $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$. As noted earlier, the observed configuration of the neutral atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$, however.

This state of affairs in turn raises the question of why two electrons (or one in the cases of chromium and copper) are elevated into a higher energy 4s orbital. One answer is because 3d orbitals are more compact than 4s, and as a result any electrons entering 3d orbitals will experience greater mutual repulsion.[26] The slightly unsettling feature is that, although the relevant s orbital can relieve such additional electron–electron repulsion, different atoms do not always make full use of this form of sheltering because the situation is more complicated than just described. One thing to consider is that nuclear charge increases as we move through the atoms, and there is a complicated set of interactions between the electrons and the nucleus as well as between the electrons themselves. This is what ultimately produces an electronic configuration and, contrary to what some educators may wish for, there is no simple qualitative rule of thumb that can fully cope with this complicated situation. For example, it appears that the most stable configuration for atoms of chromium, copper, niobium, molybdenum, ruthenium, rhodium, silver, platinum, and gold involve only moving one electron into an s orbital. The case of palladium is even more unexpected because it is the one instance for which no electrons are promoted up to the less stable s orbital. Palladium can thus be said to be doubly anomalous.

However, there is no reason for chemistry teachers and textbook authors to continue to teach the sloppy version of the *aufbau* principle. Not only does it give false predictions regarding the order of electron filling in atoms, but it also leads teachers and textbook authors to perpetuate further educational inaccuracies. It is time that the teaching of the *aufbau* and electronic configurations were carried out properly in order to reflect the truth of the matter, rather than taking a shortcut and compounding it with ad hoc assumptions. At present very few books and sources give a correct account.[27] The simple fact is that the 4s orbital fills last and so quite reasonably also ionizes first. Interestingly, the truth turns out to be simpler than the textbook fiction and the use of the sloppy version of the *aufbau*.

Anomalous Configurations

There are approximately 20 elements whose atoms do not follow the Madelung rule in that their configurations are anomalous. For example, the atom of chromium would be expected to have a configuration of [Ar] $3d^4$ $4s^2$ according to the Madelung rule; yet experimental evidence points to its being [Ar] $3d^5$ $4s^1$. Figure 9.5 shows all the atoms, which behave in this anomalous manner in the sense that their outermost s orbital does not possess an s^2 configuration.

The traditional textbook explanations for many of these anomalies tend to be ad hoc. Foremost among them is the view that chromium adopts an anomalous configuration of [Ar]$3d^5$ $4s^1$ because it thereby obtains a half-filled subshell, which is assumed to have some sort of magical stability by analogy to the stability of completely filled shells. However, there is no principle of physics that supports the view that a half-filled subshell should possess any additional stability. Even more importantly, it turns out that the possession of a half-filled subshell is neither necessary nor sufficient for an atom to display an anomalous configuration. For example, although chromium and molybdenum that lie in group 6 do indeed show both half-filled d subshells and anomalous configurations, this is not true of the other two elements in the group, namely, tungsten and seaborgium.[28] In addition, there are several transition elements for which the opposite is true, meaning that they do possess anomalous configurations although they do not have half-filled subshells. This is the case for niobium, ruthenium, and rhodium, to cite a few cases.

Recently, an intriguing explanation for these anomalous configurations has come to light, courtesy of theoretical chemist Eugen Schwarz.[29] In order to grasp this explanation, we need to consider how the electronic configuration of any atom is actually obtained from the spectrum of its gas phase atoms, and we also need to consider a particular way of obtaining the ground state of any particular atom.

The traditional approach consists of examining the spectrum of the gas phase atoms of any particular element and simply looking for the spectroscopic term of lowest energy. One then tries to identify the electronic configuration that gives rise to this spectroscopic term, which becomes identified with the ground-state configuration of the atom in question. Consider, for example, the spectrum of neutral scandium, part of which is shown in figure 9.6. In this case, the spectroscopic term of lowest energy is the one shown as 0.0000 in the fourth column. This term originates from the configuration $3d^1$ $4s^2$ as shown in the first column. In most treatments of electronic configurations this is the end of the story as far as identifying the ground-state configuration is concerned.

In more accurate work, however, one seeks the average configuration, obtained by taking an average of the energies of all the spectroscopic terms arising from each of the lowest lying electronic configurations of any atom.[30] In the spectrum shown in figure 9.6, this involves taking an average of all the terms originating from the $3d^14s^2$ configuration and comparing this energy with the average value for all the spectroscopic terms arising from the $3d^24s^1$ configuration, of which there are 15 terms in this case. The manner in which this averaging is carried out requires the use of the J, or overall quantum, number that is the result of coupling the total orbital angular momentum of the atom L with its total spin angular momentum or S.

Figure 9.7 presents the results of calculating the lowest lying configuration of the scandium atom, when carried out via this averaging procedure. In the case of this atom, the ground-state configuration is the same, namely, $3d^14s^2$, regardless of whether it is obtained in the traditional manner or by this more elaborate averaging procedure. In fact, the $3d^14s^2$ configuration is found to be almost exactly 2 eV more stable than the next configuration of $3d^24s^1$.

Configuration	**Term**	***J***	**Level (cm-*1*)**
$3d4s^2$	$^2\mathrm{D}$	3/2	0.0000
		5/2	168.3371
$3d^2(^3\mathrm{F})4s$	$^4\mathrm{F}$	3/2	11 519.9611
		5/2	11 557.6556
		7/2	11 610.2357
		9/2	11 677.3121
$3d^2(^3\mathrm{F})4s$	$^2\mathrm{F}$	5/2	14 926.061
		7/2	15 041.902
$3d4s(^3\mathrm{D})4p$	$^4\mathrm{F}^\circ$	3/2	15 672.5595
		5/2	15 756.5295
		7/2	15 881.7082
		9/2	16 026.5528
$3d4s(^3\mathrm{D})4p$	$^4\mathrm{D}^\circ$	1/2	16 009.7432
		3/2	16 021.7788
		5/2	16 141.0012
		7/2	16 210.8140
$3d4s(^1\mathrm{D})4p$	$^2\mathrm{D}^\circ$	5/2	16 022.7219
		3/2	16 096.8834
$3d^2(^1\mathrm{D})4s$	$^2\mathrm{D}$	5/2	17 012.753
		3/2	17 025.127
$3d^2(^3\mathrm{P})4s$	$^4\mathrm{P}$	1/2	17 226.025
		3/2	17 255.076
		5/2	17 307.069
$3d4s(^3\mathrm{D})4p$	$^4\mathrm{P}^\circ$	1/2	18 504.058
		3/2	18 515.665
		5/2	18 571.386
$4s^24p$	$^2\mathrm{P}^\circ$	1/2	18 711.029
		3/2	18 855.734
$3d^2(^1\mathrm{G})4s$	$^2\mathrm{G}$	9/2	20 236.877
		7/2	20 239.650
$3d^2(^3\mathrm{P})4s$	$^2\mathrm{P}$	1/2	20 681.410
		3/2	20 719.833

FIGURE 9.6 Part of the scandium neutral atom spectrum. The ground state configuration is generally taken to be the one that gives rise to the spectroscopic term with the lowest energy or $3d^14s^2$ in this case, for which the energy is given as 0.0000.

Configuration averages in scandium

d^1s^2

Term	J	E/cm^{-1}	2J+1	$E_{weighted}$	Degeneracy	$E_{average}$/cm^{-1}	$E_{average}$/eV
^2D	1.5	0.00	4	0.00	10	101.00	0.012523
	2.5	168.34	6	1010.04			$E_{average}$rel.s^1 / eV −1.99

d^2s^1

Term	J	E/cm^{-1}	2J+1	$E_{weighted}$	Degeneracy	$E_{average}$/cm^{-1}	$E_{average}$/eV
4F	1.5	11519.99	4	46079.96	90	16165.20	2.00
	2.5	11557.69	6	69346.14			$E_{average}$rel.s^1 / eV 0.00
	3.5	11610.28	8	92882.24			
	4.5	11677.38	10	116773.80			
2F	2.5	14926.07	6	89556.42			
	3.5	15041.92	8	120335.36			
2D	2.5	17012.76	6	102076.56			
	1.5	17025.14	4	68100.56			
4P	0.5	17226.04	2	34452.08			
	1.5	17255.07	4	69020.28			
	2.5	17307.08	6	103842.48			
2G	4.5	20236.86	10	202368.60			
	3.5	20239.66	8	161917.28			
2P	0.5	20681.43	2	41362.86			
	1.5	20719.86	4	82879.44			
2S	0.5	26936.98	2	53873.96			

FIGURE 9.7 Calculation to obtain the average energy of any particular configuration, taken over all contributing spectroscopic terms. Data used here differs slightly from levels fig. 9.6

But this is not true in all cases. Figure 9.8 shows the variation in the energies of the s^2, s^1, and s^0 configurations for each atom beginning with calcium and ending with copper. Clearly, as atomic number increases, the energy of the s^2 configuration shows an increase relative to that of the s^1 configuration. Whereas the s^2 configuration is considerably more stable for elements such as scandium, the energies of atomic configurations cross over each other when the atom of iron is reached. In the case of the nickel atom, the s^1 configuration is found to be approximately 1 eV lower than the s^2 configuration. These results imply that the ground-state configurations for several atoms are different from what they are generally regarded as according to the traditional approach (figure 9.9).

Returning to the theme of this chapter and the extent to which quantum mechanics explains the periodic table, we see that this alternative method for calculating electronic configurations of atoms provides a perfectly natural explanation for the so-called anomalous configurations. It could be argued that there are in fact no anomalies since one is merely seeing the result of the variation of two energies, those of the s^2 and s^1 configurations, which happen to cross at a certain point along

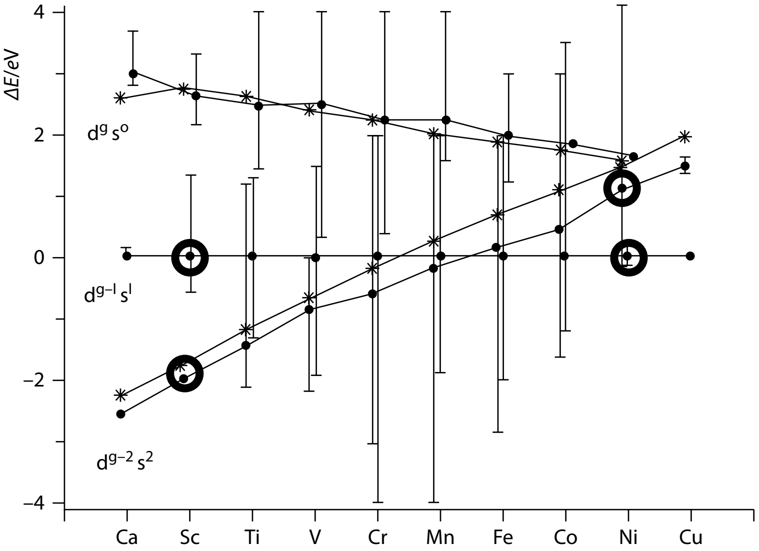


FIGURE 9.8 Variation in energies of s^2, s^1 and s^0 configurations across the first transition series. For iron and elements beyond, the s^1 configuration is more stable than s^2. The atoms of scandium and nickel have been highlighted with circles. In the case of scandium the average s^2 configuration lies lower than the s^1 configuration. In the case of the nickel atom the situation is the other way round. Small bold circles represent configurations obtained experimentally from spectral evidence. The crosses represent configuration energies obtained theoretically via the Hartree-Fock method. (Wang et al, 2006).

the first transition series. Moreover, and perhaps more pertinent to the present chapter, the energies of these configurations can be computed from first principles via the Hartree-Fock method and are found to show very similar trends, including a crossing of energies at more or less the same point along the transition series.

An Explanation for Shell Closing but Not for Period Closing

As suggested above, there is a problem with the claim that the periodic table is deductively explained by quantum mechanics. A feature that seems to generally go unnoticed is the need to assume the empirical order of shell filling rather than trying to derive it from the theory. The order in which orbitals are occupied with electrons is not derived from first principles. It is justified *post facto* and by some complex calculations.

Suppose, for example, that the Hartree-Fock method is used to compare the energies of the scandium atom with two alternative configurations: [Ar] $4s^2 3d^1$ and [Ar] $4s^1 3d^2$. This can be carried out using ordinary nonrelativistic quantum mechanics or, alternatively, by including relativistic effects. The results obtained are as shown in table 9.2.[31] In each case, the more negative the calculated value of the energy, the more stable the configuration.[32] Clearly, the inclusion of relativistic

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	*Cr*	Mn	Fe	Co	Ni	*Cu*	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	*Nb*	*Mo*	Tc	*Ru*	*Rh*	*Pd*	*Ag*	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	*Pt*	*Au*	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	*Lr*	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

La	*Ce*	Pr	Nd	Pm	Sm	Eu	*Gd*	Tb	Dy	Ho	Er	Tm	Yb
Ac	*Th*	*Pa*	*U*	*Np*	Pu	Am	*Cm*	Bk	Cf	Es	Fm	Md	No

FIGURE 9.9 The 20 traditionally regarded anomalous configurations, for which symbols are shown in italics.

effects serves to reduce the energy from the nonrelativistic value, as one would expect. In the case of scandium, it appears that both nonrelativistic and relativistic ab initio calculations correctly compute that the $4s^2$ configuration has the lower energy, in accordance with experimental data. Similar calculations do not fare so well in the case of the chromium atom, however (table 9.3). In this case, it appears that both nonrelativistic and relativistic calculations fail to predict which of these two configurations is the correct experimentally observed ground state, namely, $4s^1 3d^5$.

Looking at the calculated energies for the copper atom in table 9.4 shows that a nonrelativistic calculation sometimes gives the correct result for the lowest energy configuration. However, it also emerges that by carrying out the calculation to a greater degree of accuracy by including relativistic effects the prediction can in some cases deteriorate in that one predicts the opposite order of stabilities than observed experimentally. The lowest energy configuration for copper cannot yet be successfully calculated from first principles, at least at this level of approximation.

TABLE 9.2
Nonrelativistic and relativistic calculated energies for two configurations of scandium (in Hartree units).

$4s^2$ $3d^1$ configuration	
Nonrelativistic	–759.73571776
Relativistic	–763.17110138
$4s^1$ $3d^2$ configuration	
Nonrelativistic	–759.66328045
Relativistic	–763.09426510

One Hartree is equal to 4.3597 × 10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, one of the leading pioneers in the field of Hartree-Fock calculations. http://atoms.vuse.vanderbilt.edu/

TABLE 9.3
Nonrelativistic and relativistic calculated energies for two configurations of chromium (in Hartree units).

$4s^1$ $3d^5$ configuration	
Nonrelativistic	–1043.141755
Relativistic	–1049.24406264
$4s^2$ $3d^4$ configuration	
Nonrelativistic	–1043.17611655
Relativistic	–1049.28622286

One Hartree is equal to 4.3597 × 10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, http://atoms.vuse.vanderbilt.edu/

TABLE 9.4
Nonrelativistic and relativistic calculated energies for two configurations of copper (in Hartree units).

$4s^1 3d^{10}$ configuration	
Nonrelativistic	–1638.9637416
Relativistic	–1652.66923668
$4s^2 3d^9$ configuration	
Nonrelativistic	–1638.95008061
Relativistic	–1652.67104670

One Hartree is equal to 4.3597×10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, http://atoms.vuse.vanderbilt.edu/

The fact that copper has a $4s^1 3d^{10}$ configuration rather than $4s^2 3d^9$ is an experimental fact. The theory is, strictly speaking, accommodating what is already known experimentally. For example, the first of the two periods of 18 elements is not due to the successive filling of 3s, 3p, and 3d electrons but due to the filling of 4s, 3d, and 4p. It just so happens that both of these sets of orbitals are filled by a total of 18 electrons. This coincidence is what gives the generally given explanation its apparent credence. It does not seem to be appreciated that these are not the same 18 electrons that are "doing the occupying" as one traverses the periodic table.[33]

The Nickel Atom

The case of nickel turns out to be more interesting (table 9.5). According to nearly every chemistry and physics textbook, the configuration of this element is given as $4s^2 3d^8$. However, the research literature on atomic calculations invariably quotes the configuration of nickel as $4s^1 3d^9$. The difference occurs because in more accurate work one considers not just the lowest possible component of the ground-state term but the average of all the components arising from a particular configuration as discussed in the previous section. Nickel is somewhat unusual in that, although the lowest energy term arises from the $4s^2 3d^8$ configuration, the average energy of all the components arising from this configuration is higher than the average energy of all the components arising from the $4s^1 3d^9$ configuration. As a consequence, the $4s^1 3d^9$ configuration should be regarded as the ground state, and it is this average energy that should be compared with experimental energies. When this comparison is made, it emerges that the quantum mechanical calculations using a relativistic Hartree-Fock approach give an incorrect ground state.

Of course, the calculations can be improved by adding extra terms until this failure is eventually corrected, but these additional measures are taken only after

Table 9.5
Nonrelativistic and relativistic calculated energies for two configurations of nickel (in Hartree units).

$4s^2 3d^8$ configuration	
Nonrelativistic	–1506.87090774
Relativistic	–1518.68636410
$4s^1 3d^9$ configuration	
Nonrelativistic	–1506.82402795
Relativistic	–1518.62638541

One Hartree is equal to 4.3597 × 10^{-18} J. Note that theory predicts a $4s^2$ $3d^8$ Configuration.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, http://atoms.vuse.vanderbilt.edu/

the fact. Moreover, the lengths to which theoreticians are forced to go to in order to obtain the correct experimental ordering of terms does not give one too much confidence in the strictly predictive power of quantum mechanical calculations in this context.[34]

Back to Hund's Rule

Let us now consider the Hund principle and the manner in which it is used to try to justify the configurations of elements in the first, second, and third transitions. The elements in the first transition series are generally believed to show two "anomalous" configurations, which include a $4s^1$ orbital occupation, rather than the more common $4s^2$ configuration.[35] These atoms are those of chromium and copper, which are taken to have respective configurations of $4s^1 3d^5$ and $4s^1 3d^{10}$. The justification for the adoption of the first of these configurations is frequently given by appeal to Hund's rule of maximum spin multiplicity. It is argued that this configuration is more stable than any alternatives because it involves a half-filled d subshell. However, if the configurations of the elements in the second transition series are considered, it is clear that this form of explanation is rather ad hoc in the sense that it cannot be generalized to other transition series.

For example, the configurations of the elements in the second transition series are shown in table 9.6. Once again, this set of configurations is primarily arrived at from experimental data, although these ground-state configurations are supported by theoretical calculations in most cases. But if the possession of half-filled orbitals is the explanation for why chromium adopts a $4s^1$ configuration in the first transition series, some other factors must be operating in many cases of the second transition series. This is because many of these atoms likewise show an s^1 configuration,

TABLE 9.6
Configurations of outermost two orbitals of elements in second transition series.

Y	$5s^24d^1$
Zr	$5s^24d^2$
Nb	$5s^14d^4$
Mo	$5s^14d^5$
Tc	$5s^14d^6$
Ru	$5s^14d^7$
Rh	$5s^14d^8$
Pd	$5s^04d^{10}$
Ag	$5s^14d^{10}$
Cd	$5s^24d^{10}$

even though they do not possess a half-filled d subshell.[36] Hund's principle is essentially an empirical result. In spite of many attempts, nobody has yet succeeded in deriving the principle from quantum mechanics.[37] Of course, some plausible arguments can be given for its effectiveness, such as the claim that one is thereby minimizing the contribution from exchange terms involving repulsions between electrons. For example, a calculation can be carried out to show that, in the case of the helium atom, the triplet state (one involving two unpaired electrons) has lower energy than the singlet state where the two electrons are paired. But contrary to the standard account one encounters in textbooks, it has been shown that the reason for the greater stability of the helium triplet state is not reduced electron–electron repulsion but the greater electron–nucleus attraction that occurs in the triplet state.[38]

Choice of Basis Set

There is yet another general problem that mars any hope of claiming that electronic configurations can be predicted theoretically and that quantum mechanics thereby provides a purely deductive explanation of what was previously only obtained from experiments. In most of the configurations considered above, it has been possible to use quantum mechanics to calculate the particular configuration that possesses the lowest energy. However, in performing such calculations, the candidate configurations that are subjected to the calculation are themselves obtained from the *aufbau* principle and other rules of thumb such as Hund's principle, or by straightforward appeal to experimental data. Theoretical calculations cannot actually predict the electronic configuration for any element. There is a very simple reason for this state of affairs, which is often overlooked. The quantum mechanical calculations on ground-state energies involve the initial selection of a basis set, which in simple terms is the electronic configuration of the atom in question. Quantum mechanical calculations do not actually generate their own basis sets.[39] So, whereas the correct ground-state electronic configurations can in many cases be correctly calculated among a number of plausible options, the options themselves are not provided by the theory. This is another weakness of the present claims to the effect that quantum mechanics fully explains the periodic system, although this limitation is being addressed in some recent work.[40]

Three Possible Approaches to the Reduction of the Periodic Table

This section attempts to take stock of the various senses of the claim that the periodic system is reduced, or fully explained, by quantum mechanics.

Qualitative Reduction/Explanation of Periodic Table in Terms of Electrons in Shells

In broad terms, the approximate recurrence of elements after certain regular intervals is explained by the possession of a certain number of outer-shell electrons. This form of explanation appears to be quantitative because it deals in number of electrons but, in fact, turns out to be rather qualitative in nature. It cannot be used to predict quantitative data such as the ground-state energy of any particular atom. In order to do so, one needs to go beyond the ground-state configuration of the atom in question, and it is essential to assume that electrons also find themselves in higher energy orbitals that are not considered in the textbook configuration of the element.

In addition, it emerges that the possession of a particular number of outer-shell electrons is neither a necessary nor a sufficient condition for an element's being in any particular group. It is possible for two elements to possess exactly the same outer electronic configuration and yet not to be in the same group of the periodic system. For example, the inert gas helium has two outer-shell electrons and yet is not generally placed among the alkaline earth elements such as magnesium, calcium, and barium, all of which also display two outer-shell electrons.[41]

Conversely, there are cases of elements that do belong in the same group of the periodic table even though they do not have the same outer-shell configuration. In fact, this occurrence is rather common among the transition metal series. Consider this interesting example:[42]

Ni	[Ar] $4s^2$ $3d^8$
Pd	[Kr] $5s^0$ $4d^{10}$
Pt	[Xe] $6s^1$ 4f14 $5d^9$

In addition, the very notion of a particular number of electrons in a particular shell stands in violation of the Pauli exclusion principle, which states that electrons cannot be distinguished.[43] The indistinguishability of electrons implies that one can never state that a particular number of electrons are in any particular shell, although it is frequently useful to make this approximation. Indeed, the independent-electron approximation, as it is known, represents one of the central paradigms in modern chemistry and physics. To state the electronic configuration of an atom is to operate within this level of approximation. For example, one might state that the configurations of two randomly chosen elements are as follows:

Carbon	$1s^2, 2s^2, 2p^2$
Fluorine	$1s^2, 2s^2, 2p^5$

This kind of activity could only be considered as fully satisfactory and as indicating a theoretical deduction if such configurations themselves could be derived from quantum mechanics. However, as discussed above, electronic configurations such as those for carbon and fluorine are arrived at essentially by means of the *aufbau* principle, which is experimentally based. The configurations can be justified in terms of calculations in some cases, but they cannot be derived from first principles because the basis set, consisting of a particular set of atomic orbitals, is generally selected before any calculation can be carried out.

Ab Initio Calculations

The second approach to be considered is a far better candidate for the claim to explain the periodic table from quantum mechanics. Even if the crude notion of a particular number of outer-shell electrons for any particular atom fails to give a fundamental explanation, it should be possible to carry out detailed calculations that allow atoms to have more complicated configurations. Going to such a deeper level than the notion of a particular number of electrons in shells might thus provide a more successful explanation of the periodic system.

Ab initio calculations aim to calculate the properties of atoms and molecules starting from the fundamental equation of quantum mechanics, the Schrödinger equation for the system. The various methods utilized vary in the extent to which they are genuinely ab initio. In some cases, the methods incorporate semiempirical aspects. For example, certain integration terms that are too difficult to evaluate are replaced by quantities derived from experimental data. But the type of approach considered here is the purer variety of such calculations, where no semiempirical aspects are incorporated. My aim is to examine the extent to which such ab initio approaches provide a reduction of the periodic system.

Indeed, such an approach represents an improvement and is a better contender for the claim of a full explanation of the periodic system. In order to illustrate both the power and the pitfalls of the method, I focus on the ab initio calculation of ionization energies of atoms. In this approach, the notion of electrons in shells is used instrumentally with the knowledge that such an approximation represents only a first-order approach to calculations. If one wishes to still think in terms of electrons in orbitals, these calculations can be thought of as regarding the atom as existing in many different electronic configurations simultaneously. The ground-state configuration, so beloved of chemistry and physics textbooks, is just the leading term in an algebraic expansion for the wavefunction of the atom in question.[44]

At this level of approximation, the fact that certain elements fall into the same group of the periodic table is not explained by recourse to the number of outer-shell electrons. Instead, the explanation lies in calculating the magnitude of a property such as the first ionization energy and seeing whether the expected periodicity is recovered in the calculations. Figure 9.10 shows schematically the experimental

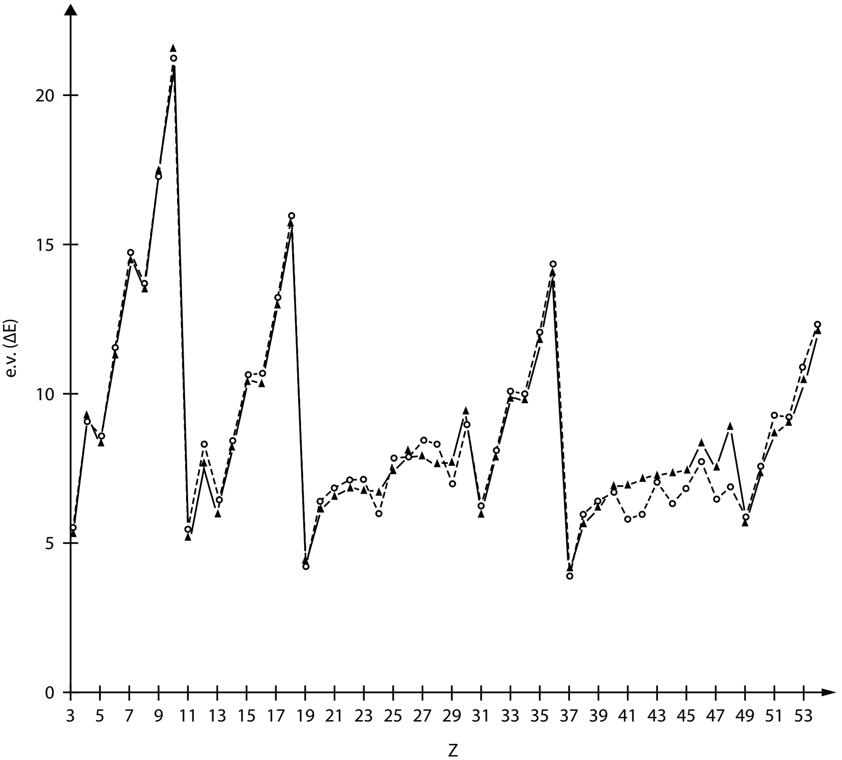


FIGURE 9.10 Calculated and observed first ionization energies of elements 3–53. Ionization energy plotted against atomic number. Circles represent experiemental values, triangles are calculated values From E. Clementi, *Computational Aspects of Large Chemical Systems, Lecture Notes in Chemistry*, vol. 19, Springer-Verlag, Berlin, 1980, p. 12. By permission from the publisher.

first-ionization energies for elements 3–53 in the periodic table, along with the values calculated using ab initio quantum mechanical methods. As is readily apparent from the figure, the periodicity is captured remarkably well, even down to portions of the graph occurring between elements in groups II and III and between groups V and VI in each period of the table. Clearly, the calculation of atomic properties can be achieved by the theory to a high degree of accuracy. The quantum mechanical explanation of the periodic system within this approach represents a far more impressive achievement than merely claiming that elements fall into similar groups because they share the same number of outer electrons.

And yet, in spite of these remarkable successes, such an ab initio approach may still be considered to be semiempirical in a rather specific sense. In order to obtain the calculated points shown in figure 9.10, the Schrödinger equation must be solved separately for each of the 50 atoms concerned. The approach therefore represents a form of "empirical mathematics,"[45] where one solves 50 individual Schrödinger equations in order to reproduce the well-known pattern in the periodicities of ionization energies. It is as if one had performed 50 individual experiments, although the "experiments" in this case are all iterative mathematical computations. This is still, therefore, not a general solution to the problem of the electronic structure of atoms.

Density Functional Approach

The third kind of approach to reducing the periodic table does not suffer from the drawback just mentioned in the case of ab initio calculations, at least not in principle. In 1926, the physicist Llewellyn Thomas proposed treating the electrons in an atom by analogy to a statistical gas of particles. No electron shells are envisaged in this model, although electrons still possess angular momentum values as they do in the electron-shell model. This method was independently rediscovered by Italian physicist Enrico Fermi two years later and is now called the Thomas-Fermi method. For many years, it was regarded as a mathematical curiosity without applications since the results it yielded were inferior to those obtained by the method based on electron orbitals. The appeal of the Thomas-Fermi method comes from the fact that it treats the electrons around the nucleus as a perfectly homogeneous electron gas and that the mathematical solution for this system is "universal" in the sense that it can be solved once and for all. This represents an improvement over any method in which one seeks to solve a Schrödinger equation for every separate atom, as in the wavefunction approach illustrated in figure 9.10.

Gradually, the Thomas-Fermi method or its modern descendants, which are known as density functional theories, have become equally powerful to methods based on orbitals and wavefunctions and in many cases can outstrip the wavefunction approaches in terms of computational accuracy. The solution is expressed in terms of the variable Z, which represents atomic number, the crucial feature that distinguishes one kind of atom from any other element. One does not need to repeat the calculation separately for each atom, but this advantage applies only in principle, as discussed below.

There is another important conceptual, or even philosophical, difference between the orbital/wavefunction methods and the required density functional methods. In the case of orbitals, the theoretical entities are completely unobservable, whereas electron density, which is featured in density functional theories, is a genuine observable.[46] Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques.[47] Orbitals cannot be observed either directly or indirectly since they have no physical reality, a state of affairs dictated by quantum mechanics. The orbitals used in ab initio calculations are just mathematical constructs that exist in a multidimensional Hilbert space,[48] while electron density is altogether different, as indicated, since it is a well-defined observable and exists in real three-dimensional space.[49]

Density Functional Theory in Practice

Most of what has been described so far concerning density theory applies in theory rather than in practice. The fact that the Thomas-Fermi method is capable of yielding a universal solution for all atoms in the periodic table is a potentially attractive feature but has not been realized in practice. Because of various technical difficulties, which are not described here, the attempts to implement the ideas originally due to Thomas and Fermi have not materialized.[50] This has meant a return to the need to solve a number of equations separately for each individual atom as one does in the Hartree-Fock method and other ab initio methods using atomic orbitals. In addition, most of the more tractable approaches in density functional theory also involve a return to the use of atomic orbitals in carrying out quantum mechanical calculations since there is no known means of obtaining the function based directly on electron density.[51] Researchers therefore generally fall back on using basis sets of atomic orbitals that yield the electron density when squared.[52]

To make matters worse, the use of a uniform gas model for electron density does not enable one to carry out accurate calculations. Instead, "ripples" must be introduced into the uniform electron gas distribution. The way in which this has been implemented has typically been in a semiempirical manner by working backward from the known results on a particular system, usually taken to be the helium atom. In this way, it has been possible to obtain an approximate set of functions that also give successful approximate calculations in many other atoms and molecules. By carrying out this combination of a semiempirical approach and retreating from the pure Thomas-Fermi ideal of a uniform gas, it has actually been possible to obtain computationally better results, in many cases, than with conventional ab initio methods using orbitals and wavefunctions.[53]

If anything, the early promise and hope offered by quantum mechanics and Paul Dirac's famous dictum that all of chemistry can be calculated from first principles has turned out to be only partly fulfilled.[54] Although calculations have become increasingly accurate, one realizes that they include considerable semiempirical elements at various levels. From the purist philosophical point of view, this implies that not everything is being explained from first principles.

As time has progressed, the best of both approaches have been blended together with the result that many computations are now performed using a mixture of wavefunction and density approaches within the same computations. This feature brings with it advantages as well as disadvantages. The unfortunate fact is that, as yet, there are no pure density functional methods that are tractable for performing calculations. The philosophical appeal of a universal solution for all the atoms of the periodic system, based on electron density rather than fictitious orbitals, has not yet borne fruit.[55]

Conclusion

The aim of this chapter has not been trying to decide whether or not the periodic system is explained by quantum mechanics *tout court*, since the situation is more subtle. It is more a question of the extent of reduction or extent of explanation that has been provided by quantum mechanics.

Whereas most chemists and educators seem to believe that the reduction is complete, perhaps there is some benefit in pursuing the question of how much is strictly explained from the theory. After all, it is hardly surprising that quantum mechanics cannot yet fully deduce the details of the periodic table, which gathers together a host of empirical data from a level far removed from the microscopic world of quantum mechanics.

It is indeed something of a miracle that quantum mechanics explains the periodic table to the extent that it does at present. But we should not let this fact seduce us into believing that it is a deductive explanation. One thing that is clear is that the attempt to explain the details of the periodic table continues to challenge the ingenuity of quantum physicists and quantum chemists and that the periodic table will continue to present a test case for the adequacy of new methods developed in quantum chemistry.[56]

Our story has now been brought up to date. From its humble beginnings as a set of isolated triads of elements, the periodic system has grown to embody more than 100 elements and has survived various discoveries such as that of isotopes and the quantum mechanical revolution in the study of matter. Rather than being swept aside, it has continued to provide a challenge to the development of ever more accurate means of calculating the basic properties of the atoms of the chemical elements. The central role of the periodic system in modern chemistry has been consolidated rather than eroded.

The reduction of chemistry to quantum mechanics has neither failed completely, as some philosophers of science have claimed,[57] nor been a complete success, as some contemporary historians have claimed.[58] The reductive enterprise has been highly successful but not to the extent of deposing the chemical facts or the quintessential discovery of chemical periodicity made by De Chancourtois, Newlands, Odling, Hinrichs, Lothar Meyer, and, most significantly, Mendeleev. Rather than undermining chemical periodicity, modern quantum physics has literally re-presented the periodic system and has provided it with a theoretical justification. More important, quantum physics has achieved this feat without assuming the imperialistic role that it is sometimes attributed.

Notes

1. Sir Karl Popper has claimed that Bohr's prediction of the chemical nature of hafnium was "the great moment when chemistry had been reduced to atomic physics." K.R. Popper, Scientific Reduction and the Essential Incompleteness of All Science, in F.L. Ayala, T. Dobzhansky (eds.), *Studies in the Philosophy of Biology*, Berkeley University Press, Berkeley, CA, 1974, pp. 259–284.

2. A. Sommerfeld, *Atombau und Spektrallinien*, Verlag & Sohn, Braunschweig, 1919.

3. It is also sometimes confusingly called the exchange force, although it does not constitute a physical force.

4. Since this book is about the periodic table of the elements, rather than compounds, the quantum theory of chemical bonding is not discussed. For a historical account of developments in molecular quantum chemistry, interested readers may consult J. Servos, *Physical Chemistry from Ostwald to Pauling*, Princeton University Press, Princeton, NJ, 1990.

5. This motivation, among others, has led to the widespread view that quantum mechanics supports an antirealistic interpretation. Such a conclusion is disputed by many philosophers, including Ernan McMullin, The Case for Scientific Realism, in J. Leplin (ed.), *Scientific Realism*, University of California Press, Berkeley, CA, 1984, pp. 8–40.

6. E.R. Scerri, Have Orbitals Really Been Observed? *Journal of Chemical Education*, 77, 1492–1494, 2000; E.R. Scerri, The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues, *Philosophy of Science*, 68 Suppl., S76–S88, 2001. See also S. Zumdahl, *Chemical Principles*, 5th ed., Houghton-Mifflin, Boston, 2005, pp. 679–680, and W.H.E. Schwarz, Measuring Orbitals: Reality of Provocation? *Angewandte Chemie International Edition* 45, 1508–1517, 2006.

7. E.g., if two sets of concentric waveforms collide with each other, the result is a series of augmentations and reductions of the intensity of the waves. If two waves find themselves differing by a whole number of wavelengths, they produce constructive interference, leading to an additive effect. Conversely, two waves that are out of phase, differing by half a wavelength, will cancel each other out. The net result of these two effects is a series of so-called fringes consisting of alternating additions and cancellations of waves or, in the jargon, constructive and destructive interference.

8. C.J. Davisson, L.H. Germer, The Scattering of Electrons by a Single Crystal of Nickel, *Nature*, 119, 558–560, 1927.

9. Although Schrödinger did not wait for any experimental support for the wave nature of electrons.

10. The first to prove the equivalence of matrix mechanics and wave mechanics was Schrödinger himself. E. Schrödinger, Über das Verhältnis der Heisenberg-Born-Jordanschen Quantenmechanik zu der meinen, *Annalen der Physik*, 79(4), 734–756, 1926; English translation in *Collected Papers on Wave Mechanics*, translated by J.F. Shearer, W.M. Deans, Chelsea, New York, 1984. A more elaborate proof was later given by J. von Neumann, *Mathematische Grundlagen der Quantenmechanik*, Springer, Berlin, 1932.

11. Just like the square of the square root of –1, which is the real number –1.

12. More technically, it is the integral of the square of the wavefunction over a finite volume element that is observable, or $\int \Psi\Psi^* \delta\tau$.

13. As described above, even this step had not been possible within the old quantum theory.

14. They did not publish their work together. First, Hartree established the basis of the method, and later, Fock made it relativistically invariant.

15. Not everybody agrees with this claim, however. See B. Friedrich . . . Hasn't It? A commentary on Eric Scerri's Paper, Has Quantum Mechanics Explained the Periodic Table? *Foundations of Chemistry*, 6, 117–132, 2004; V.N. Ostrovsky, What and How Physics Contributes to Understanding the Periodic Law, *Foundations of Chemistry*, 3, 145–181, 2001.

16. E.R. Scerri, Have Orbitals Really Been Observed? *Journal of Chemical Education*, 77, 1492–1494, 2000; E.R. Scerri, The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues, *Philosophy of Science*, 68(3), Supplement: Proceedings of the 2000 Biennial Meeting of the Philosophy of Science Association. Part I: Contributed Papers (Sep., 2001), S76–S88; P. Mulder, Are Orbitals Observable? *HYLE—International Journal for Philosophy of Chemistry*, 17(1), 24–35, 2011.

17. More correctly, the principle is stated by saying that the wavefunction for a system of fermions is antisymmetric on the interchange of any two fermions. This version correctly avoids the assignment of quantum numbers to each individual electron in a many-electron system.

18. Löwdin has expressed his views on the $n + \ell$ rule in P.-O. Löwdin, Some Comments on the Periodic System of the Elements, *International Journal of Quantum Chemistry*, 3 Suppl., 331–334, 1969.

19. This fact is also frequently downplayed in textbook accounts of the rules for obtaining electronic configurations.

20. E.R. Scerri, The Exclusion Principle, Chemistry and Hidden Variables, *Synthese*, 102, 165–169, 1995.

21. Moving to the many-electron case involves the use of analogous quantum numbers for which the usual one-electron-atom labels are retained.

22. Using the equation for the maximum capacity of any main shell, namely, $2n^2$.

23. E.R. Scerri, Transition Metal Configurations and Limitations of the Orbital Approximation, *Journal of Chemical Education*, 66(6), 481–483, 1989; L.G. Vanquickenborne, K. Pierloot, D. Devoghel, Transition Metals and the Aufbau Principle, *Journal of Chemical Education*, 71, 469, 1994.

24. C. Moore, *Atomic Energy Levels, Vol. 1,* US Bureau of Standards, Washington, DC, 1949.

25. The configuration of the chromium atom is anomalous, however, being [Ar] $3d^5 4s^1$.

26. A more sophisticated explanation is to consider the following competing configurations:

$$E(3d^14s^2) = 2E_{4s} + E_{3d} + J_{ss} + 2J_{sd} + 2J_{sd} - K_{sd} \quad (1)$$

$$E(3d^24s^1) = E_{4s} + 2E_{3d} + 2J_{sd} + J_{dd} - 2K_{sd} - K_{dd} \quad (2)$$

$$E(3d^3) = 3E_{3d} + 3J_{dd} - 3K_{dd} \quad (3)$$

Since the J_{dd} term is dominant and only (1) lacks this destabilizing term, this can be used to explain the adoption of this particular configuration. The disadvantage of this approach is that it lacks generality since the competing expressions will be different for each atom, as will all the interaction terms of the E, J, and K type.

27. S. Glasstone, *Textbook of Physical Chemistry*, 1946; D.W. Oxtoby, H.P. Gillis, A. Campion, *Principles of Modern Chemistry*, 2007; E.R. Scerri, *A Tale of Seven Elements*, 2013; S.G. Wang, W.H.E Schwarz, Icon of Chemistry: The Periodic System of Chemical Elements in the New Century, *Angewandte Chemie International Edition* 2009, 48, 3404–3415.

28. Admittedly, these heavy atoms experience relativistic effects that could conceivably influence precisely which configuration shows the greatest stability.

29. S.G. Wang, Y.X. Qiu, H. Fang, W.H.E. Schwarz (2006). The Challenge of the So-called Electron Configurations of Transition Metals, *Chemistry: A European Journal*, 12, 4101–4114.

30. Ibid.

31. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, one of the leading pioneers in the field of Hartree-Fock calculations. http://atoms.vuse.vanderbilt.edu/

32. This choice is made by convention. The energy corresponding to ionization is taken to be zero. All bound states have lower energies, and so the more negative, the more stable an energy level.

33. Of course, I am talking loosely since electrons are indistinguishable according to quantum mechanics.

34. E.g., very accurate calculations on the nickel atom include the use of basis sets that extend up to 14s, 9p, and 5d as well as f orbitals. K. Raghavachari, G.W. Trucks, Highly Correlated Systems. Ionization Energies of First Row Transition Metals Sc-Zn, *Journal of Chemical Physics*, 91, 2457–2460, 1989.

35. As I argued, nickel also has a configuration of $4s^1$ and not $4s^2$, as generally stated.

36. The possession of a half-filled subshell by any atom is neither necessary nor sufficient to ensure that an s^1 configuration is adopted.

37. A theoretical analysis of Hund's rule is given in J. Katriel, R. Pauncz, *Advances in Quantum Chemistry*, 10, 143–185, 1977. An alternative account is provided by W. Kutzelnigg, J.D. Morgan, Hund's Rules, *Zeitschrift für Physik D—Atoms, Molecules and Clusters* 36, 197, 1996.

38. R.L. Snow, J.L. Bills, The Pauli Principle and Electronic Repulsion in Helium, *Journal of Chemical Education*, 51, 585–586, 1974.

39. With the exception of some recent work on so-called universal basis sets. E.V.R. de Castro, F.E. Gorge, Accurate Universal Gaussian Basis Set for All Atoms of the Periodic Table,' *Journal of Chemical Physics*, 108, 5225–5229, 1998; A. Canal Neto, P.R. Librelon, E.P. Muniz, F.E. Jorge, R. Colistete Júnior, Some Considerations about Dirac-Fock Calculations, *Theochem*, 539, 11–15, 2001.

40. For the author's more recent views on the reduction of the periodic table, see E.R. Scerri in E.R. Scerri, G. Fisher, *Essays in the Philosophy of Chemistry*, Oxford University Press, New York, 2016.

41. However, there are several arguments that can be made in favor of placing helium among the alkaline earths. This is carried out in the left-step periodic table, e.g., G. Katz, The Periodic Table: An Eight Period Table for the 21st Century, *The Chemical Educator*, 6,

324–332, 2001: E.R. Scerri, Presenting the Left-Step Periodic Table, *Education in Chemistry,* 42, 135–136*,* 2005; The Dual Sense of the Term "Element,"Attempts to Derive the Madelung Rule and the Optimal Form of the Periodic Table, If Any, *International Journal of Quantum Chemistry*, 109, 959–971, 2009.

42. Although, as noted above, the configuration of nickel is actually $4s^1 3d^9$, contrary to what is stated in most textbooks. Even if one considers the total number of electrons in the two most energetic orbitals, they do not all show the same value.

43. This point is disputed by V. Ostrovsky, What and How Physics Contributes to Understanding the Periodic Law, *Foundations of Chemistry*, 3, 145–182, 2001; see p. 175.

44. Of course, there are methods used in ab initio work that even go beyond the orbital approximation altogether, but this is discussed further below.

45. This expression is due to philosopher of physics Michael Redhead; see M. Redhead, Models in Physics, *British Journal for the Philosophy of Science*, 31, 154–163, 1980. A similar point is made by V. Ostrovsky, What and How Physics Contributes to Understanding the Periodic Law, *Foundations of Chemistry*, 3, 145–182, 2001.

46. There is also redundancy of information in the ab initio approach, in view of the fact that it operates in 3*N* dimensions rather than the familiar three-dimensional space in which density functional theory operates.

47. The reports, starting in *Nature* magazine in September 1999, that atomic orbitals had been directly observed are incorrect. J. Zuo, M. Kim, M. O'Keefe, J. Spence, Direct Observation of d-Orbital Holes and Cu–Cu Bonding in Cu_2O, *Nature*, 401, 49–52, 1999; P. Coppens, *X-Ray Charge Densities and Chemical Bonding*, Oxford University Press, Oxford, 1997.

48. The educational implications of the claims for the observation of orbitals are addressed in other articles, and I do not dwell on the issue here.

49. This is an advantage only for a realist. The antirealist is not unduly perturbed by the fact that central scientific terms such as atomic orbitals are nonreferring.

50. P.M.W. Gill, Density Functional Theory (DF), Hartree-Fock (HF), and the Self-Consistent Field, in P. von Ragué Schlyer (ed.), *Encyclopedia of Computational Chemistry*, vol. 1, Wiley, Chichester, UK, 1998, 678–689.

51. The promise derives from some theorems proved by P.C. Hohenberg, L.J. Sham, and Walter Kohn. P. Hohenberg, W. Kohn, Inhomogeneous Electron Gas, *Physical Review B*, 136, 864–871, 1964; W. Kohn, L.J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects,' *Physical Review A*, 140, 1133–1138, 1965.

52. This statement should now be qualified in the light of recent research on orbital-free methods. V.L. Ligneres, E.A. Carter, An Introduction to Orbital Free Density Functional Theory". In Syndey Yip (ed.). Handbook of Materials Modeling. Springer Netherlands. 2005, pp. 137–148.

53. An excellent account of ab initio and density functional quantum chemistry calculations is provided in the Nobel Prize acceptance address by J. Pople, *Reviews of Modern Physics*, 71, 1267–1274, 1999.

54. Dirac's famous statement concerning the reduction of chemistry was "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. P.A.M. Dirac, Quantum Mechanics of Many-Electron Systems, *Proceedings of the Royal Society of London, Series A*, 123, 714–733, 1929, quoted from p. 714.

55. Other universal approaches to the problem of the periodic table have been pursued by Dudley Herschbach and colleagues; see S. Kais, S.M. Sung, D.R. Herschbach, Large-Z and -N Dependence of Atomic Energies of the Large-Dimension Limit, *International Journal of Quantum Chemistry*, 49, 657–674, 1994.

56. As mentioned in note 18, this problem has been recognized by some leading quantum chemists, such as Löwdin. Several attempts to solve the problem have been published. See, e.g., V. Ostrovsky, What and How Physics Contributes to Understanding the Periodic Law, *Foundations of Chemistry*, 3, 145–182, 2001. Readers may also be interested in the present author's chapter in a book based on an international conference on the periodic table: E.R. Scerri, The Best Representation of the Periodic System: The Role of the $n + \ell$ Rule and the Concept of an Element as a Basic Substance, in D. Rouvray, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Science Studies Press, Bristol, UK, 2004, 143–160.

57. J. Dupré, *Human Nature and the Limits of Science*, Clarendon Press, Oxford, 2001; J. van Brakel, *The Philosophy of Chemistry*, Leuven University Press, Leuven, Belgium, 2000 (see chapter 5 in particular).

58. B. Bensaude, I. Stengers, *A History of Chemistry*, Harvard University Press, Cambridge, MA, 1996 (see chapter 5 in particular); D. Knight, *Ideas in Chemistry*, Rutgers University Press, New Brunswick, NJ, 1992 (see chapter 12).

CHAPTER

10

ASTROPHYSICS AND NUCLEOSYNTHESIS

Having now examined attempts to explain the nature of the elements and the periodic system in a theoretical manner, it is necessary to backtrack a little in order to pick up a number of important issues not yet addressed. As in the preceding chapters, several contributions from fields outside of chemistry are encountered, and the treatment proceeds historically.

So far in this book, the elements have been treated as if they have always existed, fully formed. Nothing has yet been said about how the elements have evolved or about the relative abundance of the isotopes of the elements. These questions form the contents of this chapter. It also emerges that different isotopes show different stabilities, a feature that can be explained to a considerable extent by appeal to theories from nuclear physics.

The study of nucleosynthesis, and especially the development of this field, is intimately connected to the development of the field of cosmology as a branch of physical science.[1] In a number of instances, different cosmological theories have been judged according to the degree to which they could explain the observed universal abundances of the various elements.[2] Perhaps the most controversial cosmological debate has been over the rival theories of the big bang and the steady-state models of the universe. The proponents of these theories frequently appealed to relative abundance data, and indeed, the eventual capitulation of the steady-state theorists, or at least some of them, was crucially dependent upon the observed ratio of hydrogen to helium in the universe.[3]

Evolution of the Elements

Chapters 2, 3, and 6 discussed Prout's hypothesis, according to which all the elements are essentially made out of hydrogen. Although the hypothesis was initially rejected on the basis of accurate atomic weight determinations, it underwent a revival in the twentieth century. As mentioned in chapter 6, the discoveries of Anton van den Broek, Henry Moseley, and others showed that there is a sense in which all elements are indeed composites of hydrogen. This is so if one focuses on the fact that hydrogen contains one proton, while all other elements contain a particular number of protons bound together in their nuclei. In this chapter, I concentrate on the second sense in which Prout's hypothesis may be said to have made a comeback. The elements are now believed to have literally evolved from hydrogen by various mechanisms. One of the first people to take this possibility seriously was the English scientist William Crookes, who was also the founder and editor of the influential journal *Chemical News*.

Crookes belongs among the pioneers of the periodic system, although his name is less frequently encountered in this context than are those of precursors such as Johann Döbereiner or discoverers such as John Newlands and Dmitri Mendeleev. Crookes began by studying chemistry under A.W. Hoffmann at the Royal College of Chemistry and then under Michael Faraday at the Royal Institution, while initially working in the field of spectroscopy. Among other accomplishments, Crookes seems to have anticipated the discovery of isotopes, as demonstrated in a quotation from him in chapter 6.

In 1861, Crookes announced the discovery of a new element, thallium, which he identified through a prominent green line in its spectrum.[4] But the most important contribution made by Crookes, for the purposes of the present chapter, was his advocating the inorganic evolution of the elements:

> In the very words selected to denote the subject that I have the honour of bringing before you, I have raised a question which may be regarded as heretical. At the time when our modern conception of chemistry first dawned upon the scientific mind, the average chemist as a matter of course accepted the elements as ultimate facts.
>
> I venture to say that our commonly received elements are not simple or primordial, that they have not arisen by chance and have not been created in a desultory and mechanical manner but have been evolved from simple matters—or perhaps indeed from one sole kind of matter. . . .[5]

Crookes made a spectroscopic study of gases at low pressure that were subjected to high-voltage electric discharges. In 1879, he speculated that the plasma present in the gases treated in this manner, as well as in the stars, consisted of a fourth state of matter. Under such conditions, Crookes argued, the atoms of the elements existed as primary matter that he identified with William Prout's protyle. Seven years later, at a meeting of the British Association for the Advancement of Science, Crookes announced his theory that the chemical elements had evolved in the stars, as they cooled from such a plasma state, through the oscillation of giant electrical forces analogous to those he had studied in discharge tubes (figure 10.1). He claimed that the main oscillating electrical force had an amplitude that corresponded to a period in Mendeleev's periodic system, for example, from hydrogen to fluorine

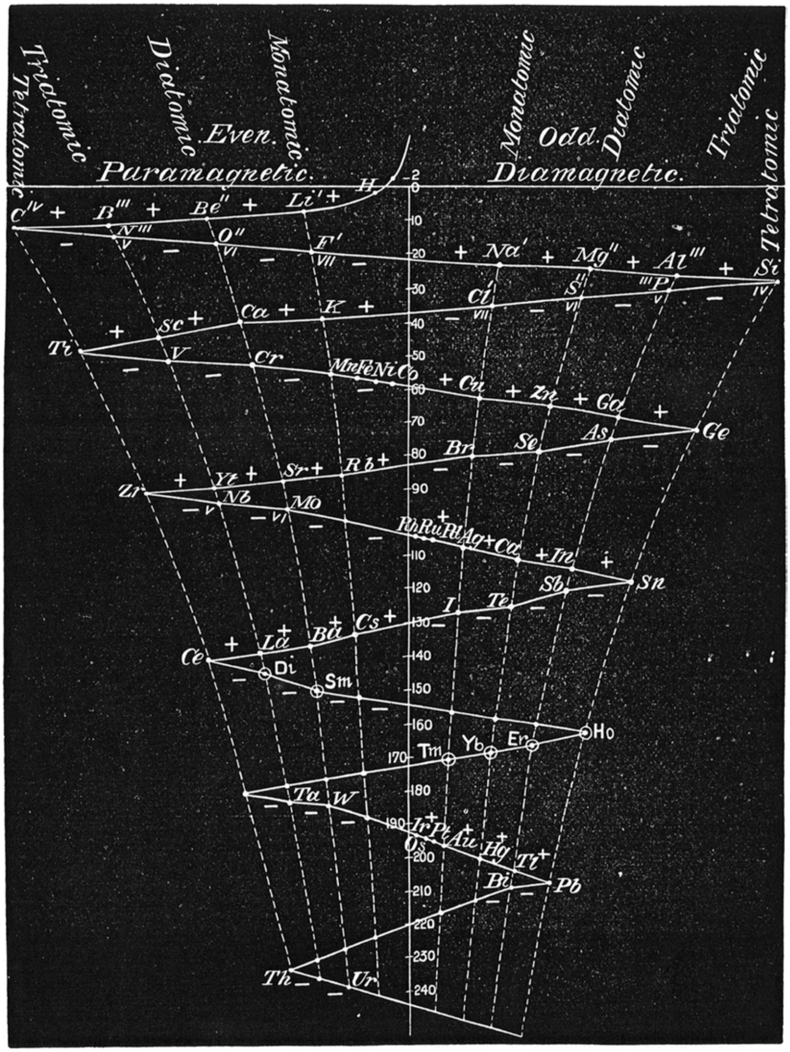


FIGURE 10.1 Crookes's electrical oscillations generating the elements. W. Crookes, *Chemical News*, 45, 115–126, 1886. Figure on p. 120.

and beyond it. A subsidiary oscillation would act in such a manner as to separate the electropositive elements from the electronegative ones. According to Crookes, the elements were formed in increasing order of atomic weight as the cosmic plasma cooled down. Such giant electrical oscillations would recur to form all the elements in the periodic table, including some that occupied new vacant spaces for elements that were still not known. Each successive amplitude became smaller, with further cooling and with increasing atomic weight, with the result that heavier elements would have more similar properties among each other than would the lighter ones.

This mechanism was illustrated by a three-dimensional pretzel-shaped periodic system, created after the discovery of the noble gases, which is still displayed at the Science Museum in London. This double helical model shows hydrogen at the top and moves downward toward the final element, uranium (figure 10.2).[6] When the noble gases were discovered in the 1890s, Crookes was quick to point out that these elements were all implied by his periodic system since they represented the centers of the giant electrical oscillations that he had published in 1886, such as the place between fluorine and sodium on his diagram (figure 10.1).

Mendeleev, however, was critical of evolutionary schemes such as these, declaring in his Faraday lecture of 1889, "The periods of the elements have a character very different from those which are so simply represented by the geometers. . . . [T]hey correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution."[7] A large number of chemists were involved in founding the field of nucleosynthesis in addition to Crookes.[8] Among them was Richard Tolman, a Caltech chemist who was also an expert in the theory of relativity and statistical mechanics. Another was Jean Perrin, a physical chemist who contributed crucially to the acceptance of atoms as real physical entities and whose early atomic model was mentioned in chapter 7. Svante Arrhenius was a Nobel Prize–winning chemist and one of the founders of physical chemistry at the turn of the twentieth

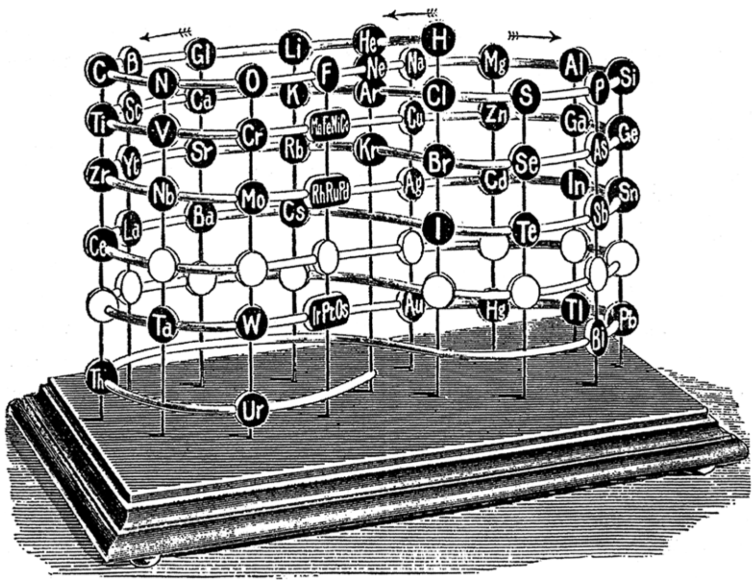


FIGURE 10.2 Crookes's periodic system. W. Crookes, *Proceedings of the Royal Society of London*, 63, 408–411, 1898, Figure on p. 409.

century. He developed a cosmological theory in which he speculated, unsuccessfully as it turned out, that the universe would not have to suffer a heat death.[9]

Similarly, Walther Nernst, another of the founding figures of physical chemistry and the discoverer of the third law of thermodynamics, speculated that radioactive atoms could be created in the ether, which was in turn associated with the zero-point energy that had recently been discovered through the new quantum mechanics. He hoped that a mechanism of continuous recycling would prevent the dreaded heat death of the universe that is generally predicted from thermodynamics.

The idea of the evolution of the elements was seriously taken up again by the astronomer Arthur Eddington, who was intrigued by Prout's hypothesis. Eddington started by suggesting that four hydrogen atoms could combine together to form atoms of helium. In an article published in *Nature* in 1920, Eddington suggested that the artificial transmutation of elements, which Rutherford had recently discovered by bombarding nuclei with protons, might also take place in the interiors of stars: "What is possible in the Cavendish Laboratory [to make atomic nuclei react] may not be too difficult in the sun."[10]

Big bang cosmology, although it did not originally bear this name, originated with the Belgian priest Georges Lemaître, who was the first to discuss the universe as having been created at a particular moment in time. At first, his theory was not taken seriously because it seemed to conflict with Albert Einstein's view of a static universe and because, as some suggested, it seemed to border on theology, especially given Lemaître's declared religious affiliations.[11]

Gradually, astronomical observations showed that the universe was indeed expanding, but whether this was occurring as a result of an initial moment of creation remained controversial.[12] The person who placed the big bang theory on a more secure foundation and, coincidentally for our story, a physicist who made the first major contribution to the theory of nucleosynthesis was the Ukrainian-born George Gamow. Gamow was also the first to bring knowledge of nuclear physics into cosmology and, as it turned out, to some considerable advantage. Broadly speaking, Gamow, along with colleagues Ralph Alpher and Hans Bethe, was able to show that the hypothesized conditions, which prevailed just after the big bang, were consistent with the synthesis of the light elements from hydrogen to beryllium.[13] They argued that the birth of the elements did not take place under equilibrium conditions but as a result of what subsequently became known as the big bang creation of the universe. The mechanism that the authors appealed to was one of neutron absorption by hydrogen atoms followed by beta decay, which could in principle be repeated to form all the elements successively. This notion depends on the fact that beta decay involves the conversion of a neutron into a proton and a beta particle, which is essentially a fast-moving electron created in the nucleus. The absorption of a neutron thus results in the formation of an element with one more proton than the previous one:

$$^1_0\text{n} \rightarrow {}^1_1\text{p} + {}^{\ 0}_{-1}\beta$$

In spite of some early successes, Gamow's theory quickly encountered a couple of major stumbling blocks concerning the formation of nuclei of masses 5 and 8. The abundance of both of these nuclei is almost completely negligible. This fact may seem harmless enough until it is appreciated that it puts a bottleneck on the formation of nuclei larger than ^{4}He by the absorption of neutrons or even protons. And if the possibility of forming successive elements by the addition of protons to lighter nuclei in the sequence is interrupted, it becomes difficult to explain the occurrence of any nuclei whatsoever with a mass heavier than 4. In addition, the nonoccurrence of nuclei of mass 8 suggests that it is impossible for two helium nuclei (mass 4) to combine together to form a composite nucleus. Of course, the gaps at mass 5 and mass 8 leave open the possibility of completely different mechanisms for the formation of heavier nuclei, but none that were even contemplated by Gamow's theory.

This impasse was partly surmounted in 1952 by Edwin Saltpeter at Cornell University. His suggestion was that a "triple alpha" mechanism could provide a means of building nuclei beyond mass number 4, as summarized in the following equation:

$$3\ {}^4\text{He} \rightarrow {}^{12}\text{C} + 2\ \gamma + 7.3\ \text{MeV}$$

Saltpeter argued that this process could very well take place in the interior of stars. In addition, he deduced that even if ^{8}Be could exist only for a small fraction of a second, this would be enough time to enable the formation of ^{12}C by an additional mechanism:

$$2\ {}^4\text{He} \rightarrow {}^8\text{Be}$$

$${}^4\text{He} + {}^8\text{Be} \rightarrow {}^{12}\text{C}^\star \rightarrow {}^{12}\text{C} + 2\ \gamma$$

Saltpeter also suggested that the ^{12}C formed by both mechanisms (triple alpha and double alpha) could then go on to capture some further alpha particles to yield ^{16}O and ^{20}Ne in accordance with the observed higher abundances of these two particular isotopes. However, Saltpeter did not have much to say on the nature of what he labeled as $^{12}\text{C}^\star$, and his theory created little impression in the astrophysical community.

The problem of how ^{12}C is formed was solved by the enigmatic British physicist Fred Hoyle (figure 10.3), who perhaps has made the greatest contributions to the question of nucleosynthesis of any person to date, as well as being one of the three architects of the steady-state cosmological theory.[14] Before describing how Hoyle solved the missing link in the triple alpha mechanism, it is necessary to return to an influential article that he published in 1946.

Although Eddington had suggested that element formation could take place in the interior of stars, the temperatures for such processes were far higher than the

FIGURE 10.3 From left to right, Margaret and Geoffrey Burbidge, William Fowler, and Fred Hoyle, coauthors of the B^2FH paper (see text).

temperatures that were assumed to exist inside of most typical stars. For example, our sun has a core temperature of a few million degrees. While these conditions can support the burning of hydrogen to form helium, they cannot begin to support the fusion of helium atoms (helium burning), which requires temperatures in the billions of degrees.[15]

Another way to appreciate the situation is to consider the following argument: In order for two nuclei to fuse together, they must approach each other at a distance approximately equal to the sum of their radii. However, such an approach is counteracted by a strongly repulsive Coulomb force, which would seem to render this process impossible. Only following the advent of quantum mechanics was it realized that such a close encounter between nuclei could still occur by means of the phenomenon of quantum mechanical tunneling, which is now believed to take place in stars. In a paper published in 1946, Hoyle sketched the essential pathways through which stellar nucleosynthesis takes place.[16]

In the course of this work, Hoyle also uncovered many important features of how stars change in the course of their lifetimes. For example, a middle-age star fuses hydrogen into helium and, in the process, loses heat as radiant light energy. Two effects then compete to determine the eventual fate of the star. On one hand, the star contracts due to the effect of the gravitational force, while on the other hand, the high temperature generated at the core of the star opposes the contraction. As the star loses its hydrogen fuel, less hydrogen burning can occur, and consequently, the temperature starts to decrease. At this point, the gravitational force begins to dominate and causes the star to contract. However, the compression that occurs causes a new increase in temperature, which acts to halt the further collapse of the star. In addition, the newly established temperature, which is invariably higher than it was previously, allows for new fusion reactions to take place. This reestablished equilibrium is only temporary, however, since the new nuclear reactions eventually run out of fuel, leading to a further contraction phase and consequently another increase in temperature.

This cycle repeats itself many times over, and each time the temperature is higher such that increasingly heavier nuclei can be made to fuse together. The essential details of Hoyle's scheme are shown in table 10.1 for a star of approximately 25 solar masses, although his calculations extended to various types of stars. In this way, different elements could be formed at different stages in the course of a star's life, culminating with the formation of the most stable nuclei of them all, those of iron.

When all the nuclear fuel is consumed, the core collapses in a very short time, followed by an explosion of the star in the form of a supernova. The explosion and the conditions generated by it lead to the formation of many heavy elements and the expulsion of this material into space. All this takes place in the outer parts of the star, while the inner core undergoes an implosion or collapse. During the collapse phase, the nuclei of iron are broken down to form neutrons, and the entire star forms a neutron star in cases where the mass is up to two to three solar masses. In heavier stars, not even the Pauli exclusion principle can halt the further collapse of the star to form a black hole.[17]

Hoyle thus obtained an almost complete solution to the problem of nucleosynthesis. What remained was to find an explanation of the second step shown in table 10.1. How could helium atoms fuse together to form carbon? As mentioned above, this was a problem that had already been confronted by Gamow and later

TABLE 10.1
Conditions needed for different stages in nucleosynthesis according to Hoyle's calculations.

Burning stage	*Density g/cm³*	*Temperature (°C)*	*Time scale*
Hydrogen	5	4×10^{7}	10^{7} years
Helium	700	2×10^{8}	10^{6} years
Carbon	2×10^{5}	6×10^{8}	600 years
Neon	5×10^{5}	1.2×10^{9}	1 year
Oxygen	1×10^{7}	1.5×10^{9}	6 months
Silicon	3×10^{7}	2.7×10^{9}	1 day
Core collapse	3×10^{11}	5.4×10^{9}	0.25 seconds
Core bounce	4×10^{14}	2.3×10^{10}	0.001 seconds
Explosive	Variable	About 10^{9}	10 seconds

Based on S. Singh, *Big Bang*, Harper Collins, New York, 2004, table on p. 388.

by Saltpeter: the lack of any plausible mechanism to form atoms of ^{12}C. Without such a mechanism, all the subsequent steps in Hoyle's table would have remained in the realm of wishful thinking.

But Hoyle succeeded in solving even this problem in an unequivocal and dramatic fashion. He predicted that a ^{4}He nucleus would combine with a nucleus of ^{8}Be to form a high-energy state (or resonance) of the carbon nucleus, contrary to all the then-known evidence on the resonance states of carbon. Hoyle was able to predict the mass and hence the energy of this new excited state by means of a wonderfully simple argument: If the mass of a ^{4}He nucleus is added to that of ^{8}Be, one obtains the mass of the hypothetical new state of carbon that can subsequently decay to form the more common ground state of carbon. The result of this calculation yields an energy of 7.68 MeV above the carbon ground state. While on a sabbatical leave at Caltech, Hoyle eventually persuaded the experimental nuclear physicist William Fowler to try to detect the new resonance state. When the experiments were conducted, they indeed revealed a new energy state at precisely 7.68 ± 0.03 MeV above the carbon ground state![18] Hoyle's triumph was complete and became further solidified when he published an even more widely cited article along with Fowler and the husband and wife team of Margaret and Geoffrey Burbidge, which became subsequently known as the B^{2}FH paper (figure 10.3).[19]

Returning to the formation of elements heavier than iron, these authors found that they formed through two main processes. First, there is a slow process of neutron capture, known appropriately as the s-process, which takes place over thousands of years, typically in red giant stars. Nuclei of zinc, for example, absorb neutrons and, following beta decay, produce nuclei of higher atomic numbers:

$$^{68}\mathrm{Zn} \xrightarrow{n} {}^{69}\mathrm{Zn} \xrightarrow{\beta} {}^{69}\mathrm{Ga} \xrightarrow{n} {}^{70}\mathrm{Ga} \xrightarrow{\beta} {}^{70}\mathrm{Ge}\ldots$$

Nuclei with masses of 230 and greater, however, are formed in the course of multiple neutron absorptions followed by multiple beta decays. This so-called r-process occurs very rapidly and in the course of supernova explosions. Elements that are ejected in supernova explosions are later incorporated into new stars, generation after generation. The presence of certain heavy elements in the sun, and the fact that solar conditions cannot support the formation of these elements, have led to the conclusion that the sun is at least a second-generation star.

Astrophysics and Cosmology: The Current View

The universe is now generally believed to have come into being about 13.7 billion years ago in the course of a cataclysmic explosion, involving matter of density 1070 g/cm^{3} and whose temperature has been set at 10^{32} K (table 10.2). This hot big bang produced matter and energy, of which just 4% is ordinary matter and the rest is present as "dark energy" and "dark matter."[20] Of the 4% of ordinary matter, 75% consists of hydrogen and 24% of helium; just 1% consists of all the other elements put together. It is therefore remarkable that all the elements other than hydrogen and helium make up just 0.04% of the universe. Seen from this perspective, the periodic system appears to be rather insignificant. But the fact remains that we live on the earth, which consists entirely of ordinary matter, as far as we know, and where the relative abundance of elements is quite different from the overall cosmic abundance. But before coming to the elements on the earth, it is interesting to consider solar abundances for a moment.

The sun is a good deal younger than the universe as a whole, being 4.55 billion years old. The percentage of hydrogen in the sun is a little less than that for the entire universe at 70%, while helium is a little higher at 28%; all the remaining elements account for 2% of the sun. The planets, including the earth, vary widely in chemical composition. While the inner planets have lost most of their gaseous atmospheres, the outer, more massive ones continue to exert an attraction on their gaseous envelopes. Indeed, Jupiter, Saturn, and Neptune are often called the "gas giants" due to their predominantly gaseous compositions. On earth, hydrogen ranks as only the 11th element in terms of abundance, or just 0.12% by mass, while helium is present only in trace amounts.[21]

TABLE 10.2
Stages in big bang cosmology.

	Time	*Temperature* (*K*)
Big bang	0	10^{32}
Protons and neutrons form	Few seconds	10^{10}
Nuclei form	3 minutes	10^{9}
Atoms form	3×10^{5} years	300

Stability of Nuclei and Cosmic Abundance of Elements

The stability of nuclei can be estimated through their binding energy, a quantity given by the difference between their masses and the masses of their constituent particles. This difference in mass gives a measure of the energy released when any particular nucleus is formed, via Einstein's famous equation $E = mc^2$. If the binding energy is divided by the mass number of any particular nucleus, one obtains the binding energy per nucleon, which provides a better means of comparing the stability of nuclei. A plot of this quantity against mass number is shown in figure 10.4. Attempts to understand this curve theoretically have been made by appealing to theories from nuclear physics.

An approximate understanding can be gained through the liquid drop model of the nucleus, as developed by Bethe, Carl Friedrich von Weiszächer, Niels Bohr, and others. In this model, the nucleus is assumed to be of uniform density like any

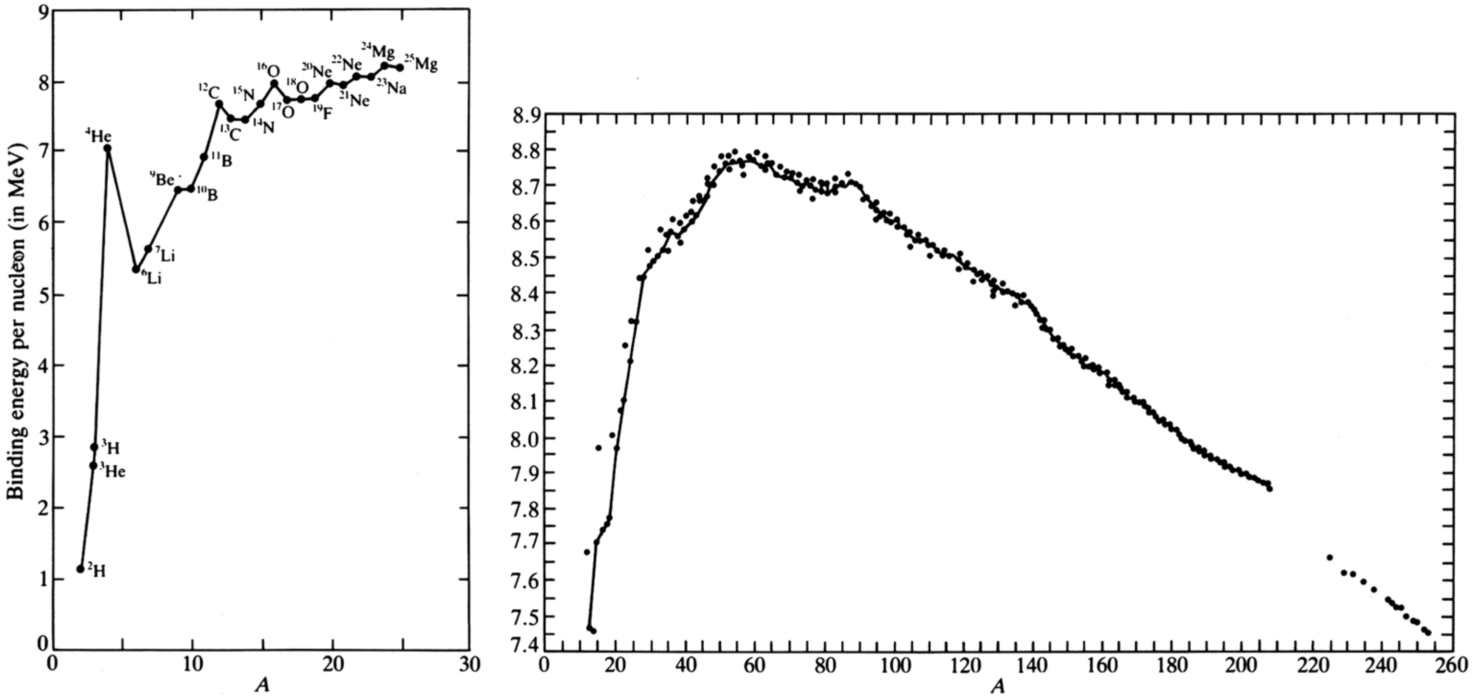


FIGURE 10.4 Binding energy per nucleon as a function of mass number for stable nuclei. Reproduced from G. Friedlander, J.W. Kennedy, E.S. Macias, J.M. Miller, *Nuclear and Radiochemistry*, John Wiley & Sons, New York, 1981, pp. 26, 27. (with permission).

drop of a uniform liquid. The objective is to explain the rapid rise in binding energy per nucleon, up to a maximum value of between 7 and 8 MeV, which occurs for iron, the most stable of all nuclei. Beyond this mass number of $A = 56$, a slow decrease occurs, indicating that nuclei become progressively less stable. Indeed, the formation of nuclei lighter than iron proceeds via exothermic processes in which energy is released. This is why it is favorable for stars to form progressively heavier elements starting from hydrogen and helium, since the energy evolved provides energy to sustain the star. Beyond iron, however, the formation of heavier nuclei occurs via endothermic processes that do not contribute to the power output of the stars.

A nucleus is stable only if the attractive nuclear force within it outweighs the repulsive force between the positive protons. The strong nuclear force, unlike the repulsive Coulomb force, operates equally between protons and neutrons and has a short range with an effect that does not exceed about 2×10^{-15} m. The observed curve in figure 10.4 can be explained in qualitative terms as the net result of combining the strong force (a) and the repulsive Coulomb force (b) in any nucleus, as shown in figure 10.5.[22]

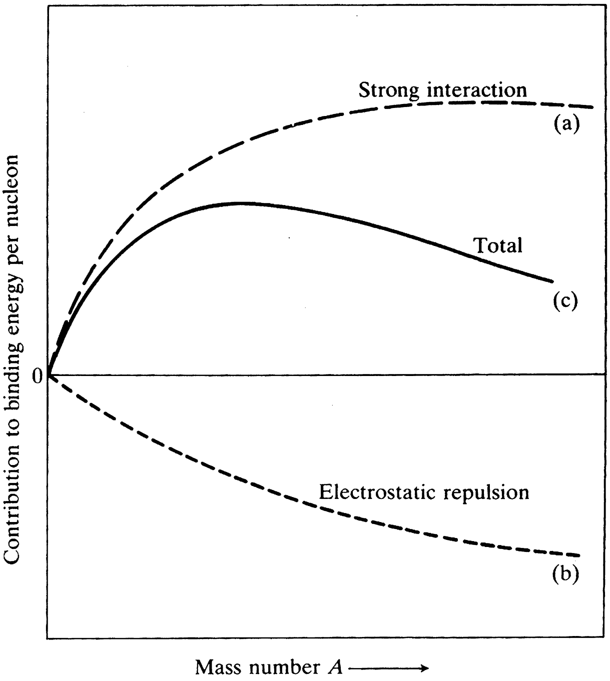


FIGURE 10.5 Separate and combined effects of strong nuclear force and repulsive Coulomb force in the nucleus. Reproduced from P.A. Cox, *The Elements*, Oxford University Press, Oxford, 1989. Figure from p. 33 (with permission).

However, the liquid drop model is powerless to explain the more detailed features within the binding energy per nucleon curve, such as the various discontinuities that are superimposed on it, reflecting the enhanced stabilities of nuclei of ^{4}He, ^{12}C, ^{16}O, ^{20}Ne, and ^{24}Mg. To explain these more subtle features, we need to consider the quantum mechanical nuclear-shell model, which bears a number of similarities to the electron-shell model as described in chapters 7 and 9.

The irregularities shown in figure 10.4 can be more easily appreciated by plotting a curve of the difference in binding energy between successive nuclei. This is carried out in a separation energy plot, which gives the energy required to remove a nucleon from any nucleus (figure 10.6). Such plots can be separately drawn for protons or neutrons and show similar general characteristics. They provide plots analogous to those of first-ionization energy plotted against atomic number, as shown in figure 9.10.

The separation energy curve for a number of nuclei, all having 70 neutrons in this case, shows a distinctive sawtooth pattern with nuclei displaying alternately more or less stable values, depending on whether the number of protons is even or odd, respectively. In addition to the sawtooth pattern, there is an overall decrease in stability following the value of $Z = 50$ as the atomic number increases. If this diagram is extended to all known nuclei, it reveals a series of maxima corresponding to especially stable nuclei at Z or $N = 2, 8, 20, 28, 50, 82$, and 126, the so-called magic numbers.[23] To some extent, the magic numbers for protons also correspond to the maxima in the plot of solar system abundance of elements (figure 10.7). These elements are $_{2}$He, $_{8}$O, $_{20}$Ca, $_{28}$Ni, $_{50}$Sn, $_{82}$Pb.[24]

The nuclear-shell model approaches this problem by approximating the forces present in the nucleus by means of a central-field potential.[25] As in the case of electrons in an atom, solving the Schrödinger equation for the nucleus yields a number of distinct energy-level solutions. The labels used for the nuclear levels are similar to those for electrons: s, p, d, and f. But there are also a number of differences in that, for example, the lowest p and d levels in the nuclear case are labeled 1p and 1d, respectively, although such combinations do not occur in the case of electrons. The nuclear energy levels can be thought of as being progressively occupied by nucleons, just like the electronic levels are progressively occupied with electrons. However, the energy levels predicted by using only the central-field approximation starting with $1s < 1p < 1d < 2s$, and so on, do not explain the occurrence of the magic numbers. The latter feat was achieved by Maria Goeppert-Mayer, Hans Suess, and Hans Jensen in the 1950s by taking into account the effect of spin-orbit coupling present between all nucleons (figure 10.8).[26]

The introduction of spin-orbit coupling between nucleons results in the splitting of energy levels. In addition, there is considerable overlap in these newly formed levels to produce the sequence shown on the right side of figure 10.8. The filling of nuclear energy levels thus proceeds in the order $1s_{1/2} < 1p_{3/2} < 1p_{1/2} < 1d_{5/2} <$ and so on. Finally, the number of nucleons that can fill any particular level is $2j + 1$ for any given angular momentum j value.

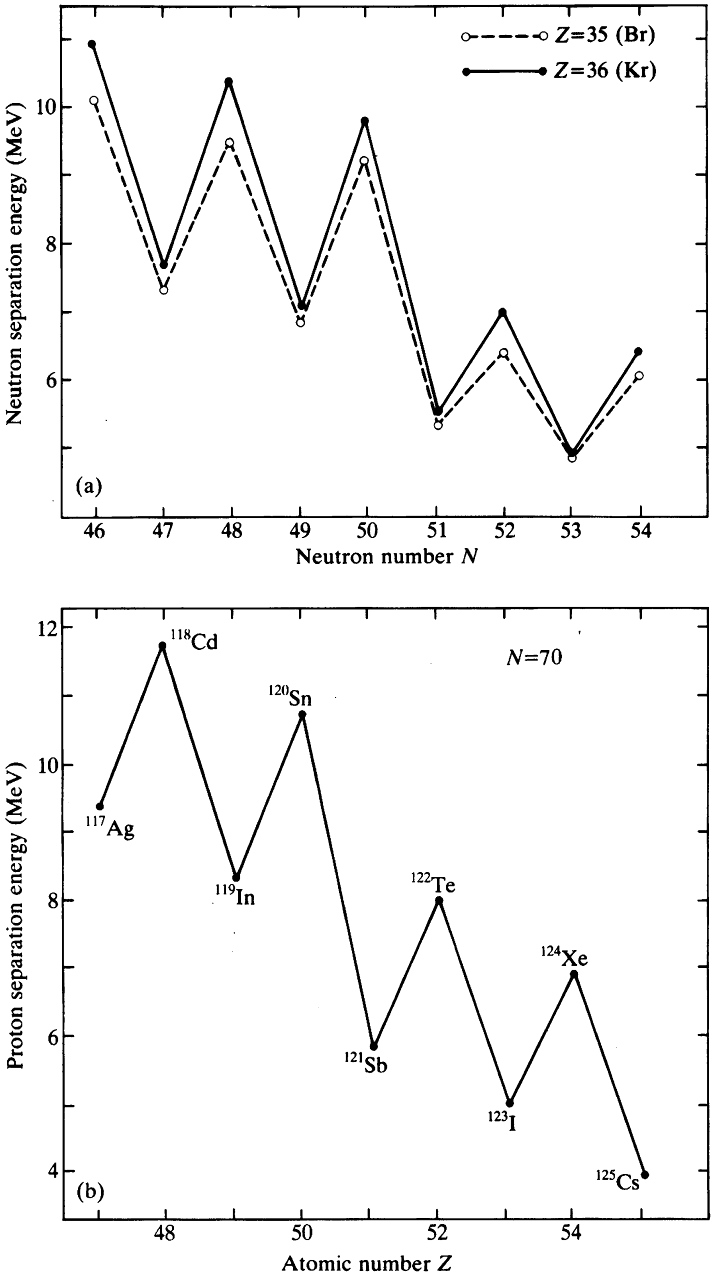


FIGURE 10.6 Separation energy plot giving energy required to remove a nucleon from any nucleus. Reproduced from P.A. Cox, *The Elements*, Oxford University Press, Oxford, 1989 (with permission).

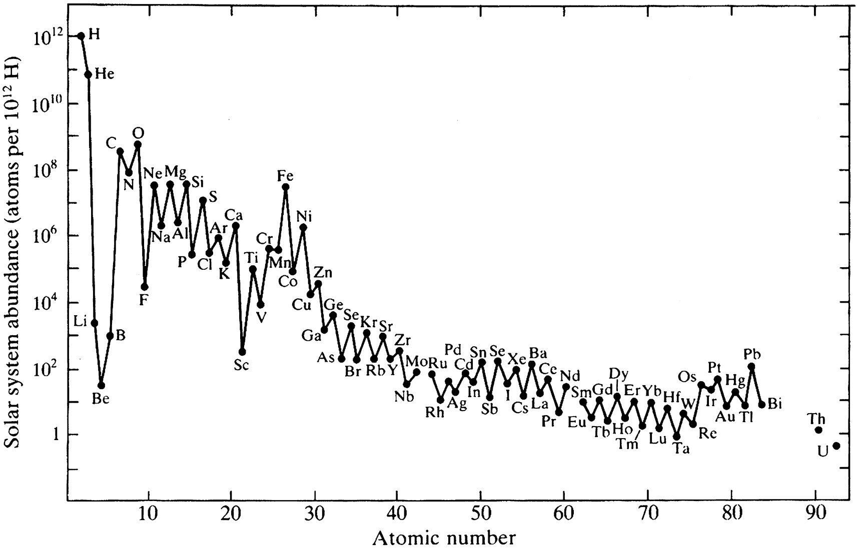


FIGURE 10.7 Relative abundance of elements in the solar system, including contributions from meteorites Reproduced from P.A. Cox, *The Elements*, Oxford University Press, Oxford, 1989. Figure from p. 17 (with permission).

In both the electronic and nuclear-shell theories, one is dealing with a many-body problem for which there is no analytical solution. As a result, the explanations provided in both cases are approximate and rely to some extent on empirical evidence, such as the precise ordering of levels. These relative orderings of levels have not been deduced from first principles, contrary to the impression created by some presentations. Indeed, problems are more severe in the nuclear case, in view of the greater complexity of the nucleus. Just as the $n + \ell$ rule is obtained empirically in the electronic case, as described in chapter 9, so the nuclear ordering by the *aufbau* principle is also obtained by appeal to empirical data.[27]

The explanation of the magic numbers by nuclear-shell theory is nevertheless a remarkable achievement in that the number of nucleons per level as well as the relationship between the various quantum numbers is deduced from first principles even if the ordering of levels is not.

Notes

1. The reader is referred to Helge Kragh, *Cosmology and Controversy*, Princeton University Press, Princeton, NJ, 1996, an excellent historical account of cosmology from which I have drawn liberally in the course of writing this section. Other good sources on nucleosynthesis are E.B. Norman, Stellar Alchemy: The Origin of the Chemical Elements, *Journal of Chemical*

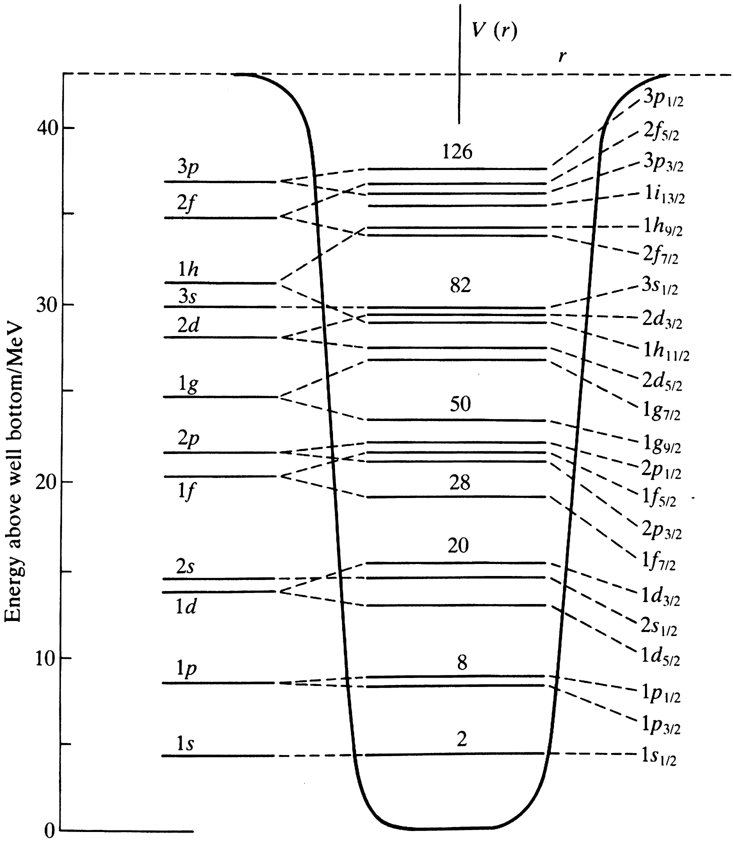


FIGURE 10.8 Energy levels obtained in nuclear-shell theory with inclusion of spin-orbit coupling as given by the Goeppert-Mayer-Jensen-Suess model. Numbers on the right represent the number of protons or neutrons in each level, with cumulative totals on extreme right. Reproduced from L. Pauling, *General Chemistry*, Dover, New York, 1970, p. 855 (with permission).

Education, 71, 813–820, 1994; P.A. Cox, *The Elements*, Oxford University Press, Oxford, 1989; and S.F. Mason, *Chemical Evolution*, Clarendon Press, Oxford, 1991.

2. One of the triumphs of the big bang theory is the successful prediction of the relative abundance of the two main isotopes of hydrogen: protium and deuterium. See chapter 20 of J.S. Rigden, *Hydrogen, The Essential Element*, Harvard University Press, Cambridge, MA, 2002.

3. Herman Bondi, one of the three founders of the steady-state theory, admitted defeat after learning of the hydrogen:helium ratio, which was interpreted as a "fossil" of the big bang. This is contrary to the popular story that it was the observation of the 3K cosmic background radiation in the 1960s that caused the steady-state theorists to throw in the towel. I am grateful to George Gale for pointing this out to me. He learned this through a series of interviews which he carried out with Bondi. Not all cosmologists have given up the steady-state theory, however. The husband and wife team of Geoffrey and Margaret

Burbidge continues to support that theory, as reported in a recent article. R. Panek, Two Against the Big Bang, *Discover*, 26, 48–53, 2005.

4. This represents an example of simultaneous discovery, as thallium was independently isolated by C.A. Lamy working in France in the same year.

5. W. Crookes, The Genesis of the Elements, *Chemical News,* 55, 83–99, 1887; quoted from p. 83.

6. For a fuller account of Crookes's periodic system, see S.F. Mason, *Chemical Evolution*, Clarendon Press, Oxford, 1991. This is also an excellent source for the history of nucleosynthesis and the study of the origin of life.

7. D.I. Mendeleev, The Periodic Law of the Chemical Elements, *Journal of the Chemical Society*, 55, 634–656, 1889 (Faraday lecture). Quoted from p. 641.

8. Whether Crookes can rightly be said to have been a chemist is debatable given his numerous interests, including spectroscopy, physics, and paranormal phenomena. The fact remains that he was initially trained as a chemist and retained a strong interest in chemistry throughout his life, including acting as the editor of *Chemical News* from when he founded it in 1859 up to the time of his death in 1919. See W. Brock, William Crookes, in C. Gillespie (ed.), *Dictionary of Scientific Biography*, vol. 3, Charles Scribner's, New York, 1981, 474–482. Brock is currently writing a scientific biography of the life of Crookes.

9. The heat death had become widely accepted on the basis of the second law of thermodynamics and the associated increase in entropy of the universe.

10. A. Eddington, The Internal Constitution of the Stars, *Nature*, 106, 14–20, 1920.

11. Lemaître was more careful and went to some length to separate his scientific beliefs from his religious ones. J.D. North, Cosmology, Creation, and the Force of History, *Interdisciplinary Science Reviews*, 25, 261–266, 2000.

12. A further early contribution to the big bang theory was provided by the work of A. Friedmann, Über die Krummung des Raumes, *Zeitschrift für Physik*, 10, 377–386, 1922.

13. Bethe had not really participated in this research, but Gamov asked him to join the authors because the names of Alpher, Bethe, and Gamov would make for a nice prank. The paper has indeed become rather famous as the αβγ paper. R.A. Alpher, H. Bethe, G. Gamov, The Origin of the Chemical Elements, *Physical Review*, 73, 803–804, 1948.

14. Two interesting biographies of the life of Hoyle have recently been published: Simon Mitton, *Conflict in the Cosmos: Fred Hoyle's Life in Science*, Joseph Henry, Washington, DC, 2005; Jane Gregory, *Fred Hoyle's Universe*, Oxford University Press, Oxford, 2005.

15. More recently, some direct evidence for hydrogen burning in the sun has become available through the study of solar neutrinos. K.S. Hirata et al., Observation of Neutrino Burst from the Supernova SN1987A, *Physical Review D*, 44, 2241–2260, 1991.

16. F. Hoyle, The Synthesis of the Elements from Hydrogen, *Monthly Notices of the Royal Astronomical Society*, 106, 343–383, 1946.

17. The term "black hole" was coined some time later by the physicist J.A. Wheeler.

18. F. Hoyle, D.N.F. Dunbar, W.A. Wenzel, W. Whaling, A State in C^{12} Predicted from Astrophysical Evidence, *Physical Review*, 92, 1095, 1953. This much-cited paper was in fact a brief announcement made at a conference, and it took up a mere 16 lines in a page arranged in two columns, the equivalent therefore of just eight lines of text. Hoyle's prediction is widely regarded as the only successful application of the anthropic principle, the notion that nature is the way that it is because this allows us to exist. Hoyle had reasoned that the resonant state of carbon had to exist since beings like us are made largely of carbon and are able to pose the question as to the formation of the element carbon.

19. Only Fowler was awarded the Nobel Prize for his work in nucleosynthesis, although it is generally agreed that the core of the discovery belonged to Hoyle. Many observers believe that Hoyle's combative style cost him a share in the Nobel Prize.

20. C. Seife, What Is the Universe Made Of?, *Science*, 309, 78, 2005.

21. For a very interesting article on how the field of geochemistry and in particular the work of Victor Goldschmidt influenced the early development of nuclear physics, see H. Kragh, An Unlikely Connection: Geochemistry and Nuclear Structure, *Physics in Perspective*, 2, 381–397, 2000.

22. Strong nuclear forces are due to nearest-neighbor interactions. In the case of the light nuclei, a greater proportion of nucleons are at the surface, and so the overall force is of greater magnitude. In the case of heavy nuclei, however, the contribution is almost constant since most nucleons can be considered as being in the "interior" of the nucleus, and so they experience the maximum number of 12 nearest-neighbor interactions.

23. The value of 126 is only experimentally realized for neutrons, given that the largest stable nuclei formed thus far have Z-values in the 110s.

24. In addition, four of these elements have "doubly magic" nuclei since they have magic numbers with respect to both protons and neutrons. The doubly magic nuclei are ^{4}He, ^{16}O, ^{40}Ca, ^{208}Pb.

25. In the case of electrons in an atom, the force can be considered to be literally centrally directed, since it results from the attraction due to the central nucleus. In the nuclear analogue, each nucleon acts on every other one, and yet one can usefully assume a centrally directed field, even though this is physically not the case.

26. Spin-orbit coupling also occurs in atoms but to a far lesser extent and is significant only for heavy atoms.

27. There are several more sophisticated approaches than nuclear-shell theory, but the empirical nature of the ordering of levels is a common feature among them.

CHAPTER

11

THE SEVEN LAST INFRA-URANIUM ELEMENTS TO BE DISCOVERED

The term "infra-uranium," meaning before uranium, is one that I have proposed by contrast to the better-known term transuranium elements that are discussed in the following chapter.[1] The present chapter concerns the last seven elements that formed the missing gaps in the old periodic table that ended with the element uranium. After Moseley developed his X-ray method, it became clear that there were just seven elements yet to be isolated among the 92 naturally occurring elements or hydrogen (#1) to uranium (#92).[2] This apparent simplicity is somewhat spoiled by the fact that, as it turned out, some of these seven elements were first isolated from natural sources following their being artificially created, but this raises more issues that are best left to the next chapter of this book. The fact remains that five of these seven elements are radioactive, the two exceptions being hafnium and rhenium, the second and third of them to be isolated.[3]

Element 91—Protactinium

The first of the seven final infra-uranium elements to be discovered was protactinium, and it was one of the lesser-known predictions made by Mendeleev. In his famous 1896 paper, Mendeleev indicated incorrect values for both thorium (118) and uranium (116). (See figure 1.6.) A couple of years later, he corrected both of these values and showed a missing element between thorium and uranium (figure 4.4). In doing so, Mendeleev added the following paragraph, in which he made some specific predictions.

> Between thorium and uranium in this series we can further expect an element with an atomic weight of about 235. This element should form a highest oxide R_2O_5, like Nb and Ta to which it should be analogous. Perhaps in the minerals

Meitner	Hevesy	Noddacks	Segrè	Perey	Segrè	Marinsky
91	72	75	43	87	85	61
Pa	Hf	Re	Tc	Fr	At	Pm
1917	1923	1925	1937	1939	1940	1945

FIGURE 11.1 The seven elements in chronological order of discovery, and their leading discoverers.

> which contain these elements a certain amount of weak acid formed from this metal will also be found.[4]

The modern atomic weight for eka-tantalum or protactinium is 229.2. The apparent inaccuracy in Mendeleev's prediction is not too surprising, however, since he never knew that protactinium is a member of only four "pair reversals" in the entire periodic table. This situation occurs when two elements need to be reversed, contrary to their atomic weights, in order to classify them correctly. The most clear-cut case of this effect is that of tellurium and iodine, as discussed in chapter 4. As has already been mentioned, one of the most important benefits of Moseley's research in 1914 had been a categorical resolution of such cases. As Moseley showed, the more correct ordering principle for the elements is atomic number and not atomic weight.

Mendeleev's brief predictions on element 91, which became known as protactinium, were approximately fulfilled since the element does indeed show an analogy with tantalum in forming Pa_2O_5 as its highest and most stable oxide. However, protactinium also shows a horizontal analogy with thorium and uranium by exhibiting the +4 oxidation state, a fact that Mendeleev does not seem to have anticipated.[5] Moreover, as he correctly predicted, protactinium does indeed occur with uranium, and more specifically in pitchblende, the mineral from which it was isolated by Lise Meitner in 1917.

Early History

William Crookes, the well-known London-based chemist–inventor and journal editor, was the first to discover what he believed to be Mendeleev's eka-tantalum, but he was unable to isolate it. Crookes described his research in an article in the *Proceedings of the Royal Society of London* for 1899–1900. It is worth pausing to consider the state of research into radioactivity at the turn of the twentieth century, much of which was carried out in France on uranium, an element that had first been reported in 1789 by Martin Klaproth working in Berlin.

Klaproth also gave the element its name in recognition of the discovery of the planet Uranus by William Herschel just eight years before. In fact, Klaproth had isolated uranium oxide, UO_2, rather than the element itself. The isolation of the

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	*Tc*	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	*Hf*	Ta	W	*Re*	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	*At*	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

La	Ce	Pr	Nd	*Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	*Pa*	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 11.2 The positions of the seven elements shown in italic letters on a medium-long periodic table.

88	89	90	91	92
Ra	Ac	Th	Eka-Ta	U
1898	1899	1815	1917	1789
Curies	Debièrne	Berzelius	Meitner	Klaproth

FIGURE 11.3 Fragment periodic table showing relative positions of elements 88 to 92, and their leading discoverers.

element took a further 50 or so years, before it was achieved by Eugène Peligot, working in France in 1841. More than a century passed between Klaproth's original "discovery" of UO_2 and the further discovery, by Henri Becquerel, that uranium possesses the remarkable property of radioactivity (chapter 6). The French tradition for work on radioactivity was carried forward by Marie and Pierre Curie, who together also isolated two other elements, polonium and radium, which turned out to be far more radioactive than uranium, followed very soon afterward by another radioactive element, actinium, which was also discovered in France, by André Debièrne (figure 11.3).

The Search for the Mother of Actinium and the Discovery of Brevium

The work on UX, as Crookes called his prematurely discovered element 91, was taken up by a number of researchers in 1913. These chemists were mainly engaged in clearing up the confusion of many newly discovered radioactive elements or in determining whether or not they were really elements at all. While the concept of isotopy was just beginning to be clarified, by the likes of Frederick Soddy, Kasimir Fajans, and Ernest Rutherford, it had not yet been realized that atomic number was a more correct ordering principle than the atomic weights of elements.

As a consequence, it was not known how many elements existed between lead and uranium or indeed whether the periodic table remained valid at such high values of atomic weight. The uncertainty was heightened by the fact that the rare earth elements could not be accommodated within the main body of the periodic table and so needed to be listed separately.[6]

In the course of this uncertainty, the element actinium remained mysterious and was perhaps the least understood of the recently discovered radio-elements, with an as yet unknown atomic weight. In addition to having an ambiguous chemistry, the value of its half-life was also in dispute. It was known that actinium might be the start of one of the three important radioactive decay series and that the element was descended from uranium. Furthermore, actinium was always found in uranium-bearing minerals, although the relationship between the two elements remained unclear.

As a result, the search was begun for the origin of actinium, or as it was termed by some, the "mother of actinium." According to Lise Meitner and Otto Hahn, working in Berlin, the aim was

> [t]o find that substance . . . the starting point for the actinium series, and to determine whether and through which intermediates actinium is derived.[7]

At about the same time, Fajans, working in Karlsruhe, Germany, and Soddy, working in Glasgow, Scotland, announced the displacement laws that aided the efforts aimed at understanding the profusion of new elements and decay products that were being discovered.

The displacement laws stated that an element undergoing α decay would produce another element with a charge of two units lower. On the other hand, an element undergoing β decay resulted, somewhat surprisingly, in a product with a charge of one unit higher (chapter 6). Partly on the basis of these radioactivity displacement rules, several radio-elements were successfully placed in the periodic table, such as Curie's radium, which showed a divalency similar to that of barium and was therefore safely assigned to group II. Meanwhile, the chemistry of thorium pointed to tetravalency and meant that the element should be placed in group IV, while the hexavalency of uranium meant that it belonged in group VI.[8]

Although the placement of actinium remained doubtful, Soddy, Meitner, Hahn, and Fajans all concluded that the element belonged to group III. This sequence of elements that appeared to be homologous to the third row of the transition metals therefore showed a conspicuous gap representing a pentavalent element that was expected to have properties similar to tantalum in group V of the periodic table (figure 11.4). This was the element that would become protactinium.

Drawing on the displacement rules, the researchers clearly saw that actinium could form in two ways. Either it was the daughter product of radium, following β decay, or else it was formed by the β decay of the suspected new group V element, or eka-tantalum as it was dubbed by Soddy. In a *Nature* article published in 1913, Soddy concluded that actinium was probably formed from the suspected new element rather than from radium, since radium had never been found together with actinium (figure 11.5).

Groups II	*III*	*IV*	*V*	*VI*
Ra	Ac	Th	?	U

FIGURE 11.4 Fragment of the periodic table showing the original placement of the elements radium to uranium inclusive.

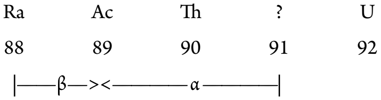


FIGURE 11.5 Two paths to the formation of actinium from radium by β decay or from the suspected new element by A decay. Although atomic numbers are used to identify the elements, the concept had not yet solidified in 1913.

A few months earlier, Fajans and Oswald Helmuth Göhring in Karlsruhe had discovered UX_2—a daughter product formed from the β emission of $UX_{1,}$ which in turn had been identified as an isotope of thorium. Reference to figure 11.2, together with the displacement laws, shows that UX_2 was the suspected new element or at least one isotope of it. It could therefore be argued that credit for an early discovery of element 91 belongs to Fajans and Göhring. Although Crookes may have worked with UX, he did not identify a new element, whereas Fajans and Göhring, using the displacement laws, could rightly claim to have discovered the element. Moreover, they confirmed their finding by carrying out chemical tests showing that the suspected new element could be separated from its parent thorium mineral by the use of tantalic acid, thus establishing a chemical analogy with the element tantalum.

Fajans and Göhring named their element brevium because of its very short half-life of 1.17 minutes. But the brevity of this half-life has meant that this element name has not survived, due to a radiochemical convention that the name of an element should be given to the discoverers of a stable isotope rather than an unstable one. As it turned out, a far more stable isotope of the new element was to be discovered a few years later. According to Fajans and Göhring, brevium was a β emitter that formed an isotope of uranium (^{234}U). This simply meant that it was not the mother of actinium. Although element 91 had been discovered in a very short-lived form, the more pressing problem of the origin of actinium had not been solved.

Soon afterward Meitner and Hahn in Berlin proposed another mechanism for the formation of actinium from the suspected new element: namely, that when the branching of the uranium series takes place at uranium-X, two simultaneous β-ray changes occur. These decays would produce two eka-tantalums, one being the known short-lived brevium and the other a still unknown long-lived α-ray-producing element that would be the parent of actinium. They also claimed that this was the only other alternative remaining to be tested and that the question should not be difficult to settle by experiment.

Indeed, this is exactly how Hahn and Meitner succeeded in discovering a long-lived isotope of the new group V element.

The Discovery of Protactinium

The discovery of a long-lived isotope of the suspected element in group V, or eka-tantalum, is attributed to Lise Meitner (figure 11.6) and Otto Hahn, although it is clear from the correspondence between them that the vast majority of the work was carried out by Meitner. Although Meitner and Hahn had recently moved into the Kaiser Wilhelm Institute for Chemistry in Berlin, Hahn would soon go off to fight in the First World War, leaving Meitner to carry out all experiments on her own. Given the weakness of the radioactivity associated with the mother of actinium, it was fortunate that Meitner and Hahn had recently moved into a new

FIGURE 11.6 Austrian postage stamp depicting Lise Meitner. Courtesy of Professor Dainel Rabinovich of University of North Carolina, Charlotte, NC.

laboratory, since their former lab had become contaminated by five or so years of work on radioactive isotopes. Meitner, in particular, went to great lengths to instruct all students and technicians to adhere to strict procedures in their new laboratory in order to avoid radioactive contamination.

Meitner and Hahn tackled the problem through two approaches. First, they worked with uranium salts, which had been extracted some 25 years previously. The second approach involved some cruder pitchblende, an ore that contained uranium and several other radio-elements. In both cases, the sought-for slow α decay was masked by more rapid decays due to thorium and polonium. Meitner and Hahn realized that they would need to monitor their samples for several years, so that the extraneous decay would decrease to reveal the much slower decay due to the mother of actinium. The prepared samples were therefore mounted under electroscopes and left for periods of several years.

In 1914, the war broke out, and Hahn was immediately conscripted and served in a notorious poison gas unit headed by Fritz Haber. Meanwhile, Meitner volunteered her services as an X-ray nurse, but after a short spell she grew tired of such work and returned to the institute in Berlin. Although she found that others had helped themselves to much of her equipment, none of the electroscopes from the experiments searching for eka-tantalum had been removed. In a letter to Hahn, she wrote,

> The Haber people treat us, of course, like captured territory—they don't take what they *need* but what they *like*. Who will guarantee that they won't come over here, and then everything will be lost. . . . I shall do everything to prevent it, we have had measurements running for such a long time.[9]

In March of 1918, Meitner and Hahn submitted an article entitled "The Mother Substance of Actinium, a New Radioactive Element of Long Half-Life," which included the following claim:

> We have succeeded in discovering a new radioactive element, and demonstrating that it is the mother substance of actinium. We propose, therefore, the name protoactinium.[10]

Rather surprisingly, Fajans seems to have readily given up his claim in the face of Meitner and Hahn's article of 1918. Whereas Fajans's brevium had a half-life of just 1.7 minutes, the Meitner-Hahn isotope had a relatively gargantuan half-life of 32,500 years! Clearly, there was no contest, and Fajans felt compelled to concede his claim to the discovery of the element.

A third set of contenders consisted of the Scottish team of Soddy and his colleague John Arnold Cranston. In fact, Soddy and Cranston, having submitted their paper in December 1917, actually beat Hahn and Meitner, who sent their paper to the German paper *Physikalische Zeitschrift* in March 1918. Whereas Fajans had observed brevium, which is the very short-lived isotope ^{234}Pa, Soddy and Cranston as well as Meitner and Hahn had observed the exceedingly long-lived isotope of ^{238}Pa. However, the team from Scotland had only formed a very small amount of the isotope and had not been able to characterize its properties to anywhere the same degree as Meitner had. To their credit, Soddy and Cranston also readily conceded priority to Meitner and Hahn.[11]

Element 72—Hafnium

The story concerning the discovery and isolation of element 72 bears all the characteristics of controversy and nationalistic overtones that characterize several of the last seven infra-uranium elements. On one hand, it seems odd that so much controversy should be associated with these elements, given that Moseley's method had apparently provided a categorical means through which they could be identified, as well as a way of knowing how many elements remained to be discovered. On the other hand, perhaps it was because the problem of the missing elements became so clearly focused on a few elements, with known atomic numbers, that the stakes became higher when it came to their discovery.

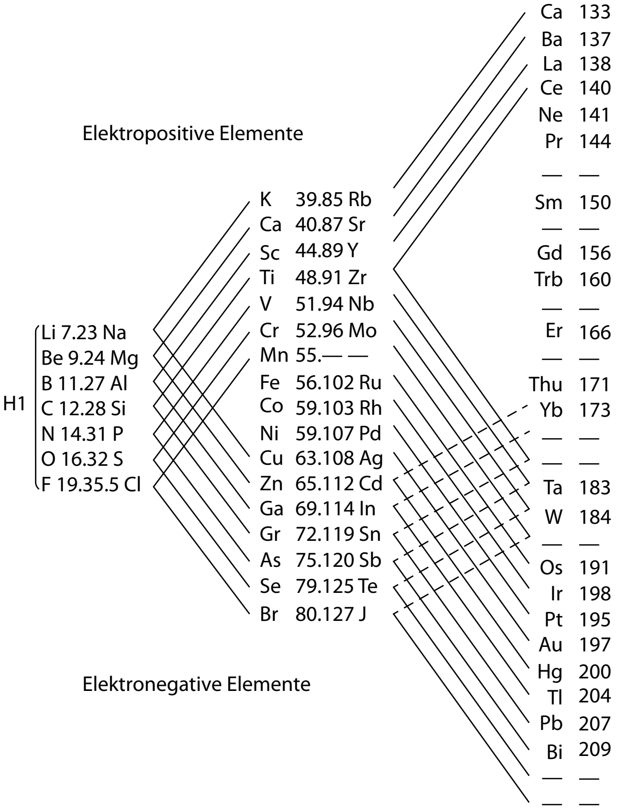


FIGURE 11.7 Thomsen's pyramidal periodic system. J. Thomsen, Systematische Gruppierung der chemischen Elemente, *Zeits für Anorgische Chemie*, 1895, 9, 190 – 193.

Element 72 was clearly anticipated even in Mendeleev's earliest table of 1869, although he could not have identified it as such. As figure 1.6 shows, Mendeleev considered that an as yet undiscovered element with an atomic number of 180 should be a homologue of zirconium. (The modern accepted value is 178.50.) The association with zirconium may not seem very significant, and yet it amounts to Mendeleev predicting that this element would be a transition metal rather than a rare earth, a point that would be much debated in the early twentieth century.

Sometime later, Julius Thomsen, a chemistry professor at the University of Copenhagen, published a periodic table in which he also included a missing element that was a homologue of zirconium (figure 11.7).

Indeed, the general consensus among chemists was that an element should exist before tantalum and that it would be a homologue of zirconium. The problem was that a further two elements, now numbered 70 and 71, respectively, were also missing at this time.

These two elements were first isolated in 1907 by two independent researchers. The first was Georges Urbain, a leading French chemist of the era, who specialized in experimental work on the rare earth elements. By analyzing the element ytterbium, which had been previously identified by Charles Marignac, Urbain claimed to have found two elements instead of one and called them neoytterbium (new ytterbium) and lutecium, respectively.[12] The second claim for the discovery of elements 70 and 71 came from the Austrian chemist Carl Auer von Welsbach, who suggested calling the elements aldebaranium and cassiopium. But it was Urbain who was eventually credited with the discovery of both elements and who won the right to name them, although the names were later changed so that neoytterbium reverted to ytterbium and the spelling of lutecium was changed to lutetium.[13]

Element 72

The connection of these discoveries with that of element 72 began to develop after this point because Urbain began to suspect that there might even be a third element lurking in Marignac's ytterbium. In 1911, Urbain announced the discovery of what he believed was this third rare earth and chose to call it celtium.[14]

Soon afterward, Henry Moseley developed his X-ray method for identifying elements and for predicting precisely which elements remained to be discovered (chapter 6). In order to justify his claim of the discovery of a third element, Urbain traveled from Paris to Oxford so that Moseley might carry out his definitive test. After just a couple of days, Moseley concluded that Urbain's sample was not in fact the missing element in question, and so Urbain abandoned his claim.

Very little concerning element 72 took place for almost 11 years, until Urbain teamed up with the X-ray spectroscopist Alexandre Dauvillier,[15] who reexamined Urbain's 1911 sample and claimed to have discovered two faint X-ray lines lying almost exactly as predicted on the basis of Moseley's law. However, it would seem that others could not even see these lines. For example, Manne Siegbahn, a leading spectroscopist who had further developed Moseley's methods, examined the Dauvillier plates and concluded that no lines were actually present.

Meanwhile, theoretical physicists had been approaching the problem from a different direction. On the basis of his atomic theory, Niels Bohr concluded that element 72 should not be a rare earth element but a quadrivalent transition element. His reasons for doing so were not entirely theoretical, and he admitted as much, along with citing the work of Julius Thomsen, as grounds for thinking the element should be a transition metal analogous to zirconium. He also cited the British chemist Charles Bury, who had independently concluded that element 72 was not a rare earth but an element analogous to the transition metal zirconium.

Two researchers, Dutchman Dirk Coster and Hungarian György von Hevesy (figure 11.8), working at Bohr's institute in Copenhagen, then decided to try to

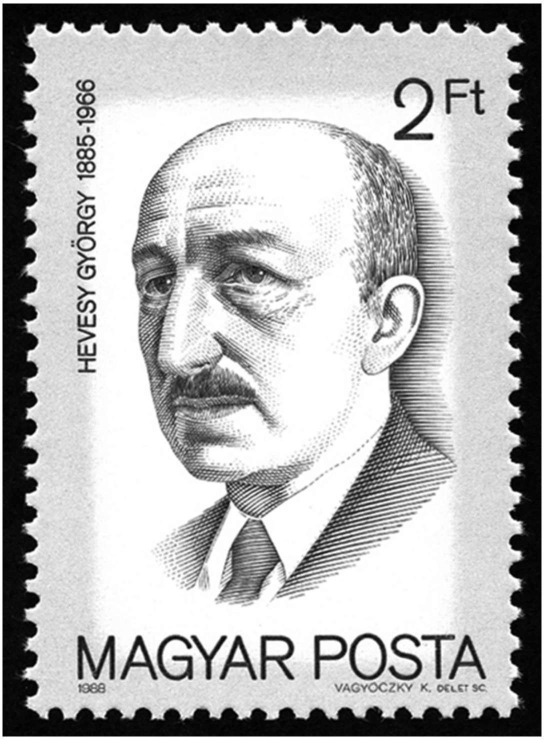


FIGURE 11.8 Georg Hevesey, one of the discoverers of hafnium. Courtesy of Professor Daniel Rabinovich of Department of Chemistry, University of North Carolina, Charlotte, N.C.

settle this question experimentally. On the basis of the older chemical predictions and Bohr's more recent predictions, they argued that if the new element were present, it should perhaps occur along with zirconium. By working with some Norwegian zirconium ores, they succeeded in observing not just two, but six, X-ray lines that were in far better agreement than Urbain's with respect to the frequencies expected on the basis of Moseley's law. They also proposed to name the element hafnium from the Latin name for Copenhagen (hafnia), the city in which the element had first been detected.[16] Coster and Hevesy also criticized the claims of Dauvillier and Urbain, pointing out that the two French lines were not close enough to the expected frequencies.

The first published reaction to the Coster and Hevesy article announcing the discovery of hafnium came from London rather than from Urbain and Dauvillier in Paris. Alexander Scott, a chemist and mineralogist from the British Museum in London, had analyzed some samples of black sand from New Zealand between the years 1913 and 1915 and believed that he had discovered a new element. Although he had not published his findings, he was now claiming to have been the first to have discovered element 72. Scott proposed to call his element oceanium, after oceania, the region from which the mineral sample originated. The further basis for his claim was that he believed he had obtained the atomic weight of the element as 144.[17]

However, Coster and Hevesy could not find any sign of a new element. Out of politeness to Scott, they nevertheless offered to continue working on the black sand in order to search for other possible new elements such as the still missing elements 61 and 75. It was several years before Scott finally withdrew his claim. But even then the British press continued to argue the case for oceanium, including a rather patriotic editorial in *The Times* of London.

> Science is and doubtless should be, international, but it is gratifying that the chemical achievement, the most important since the late Sir Wm. Ramsay isolated helium in 1895, should have been the work of a British chemist in a London laboratory. The element 72 which was thought to be, if existing, exceedingly rare and the properties of which were calculated by Danish chemists was actually discovered by Alexander Scott.[18]

More significantly perhaps, Coster and Hevesy's paper sparked one of the most bitter and acrimonious priority disputes in twentieth-century science. On one side of the debate were the French scientists, including Dauvillier, Urbain, and Maurice de Broglie. Moreover, a number of British chemists defended the French claim and persisted in calling the element celtium for quite a long period of time. The only significant supporter of the Danish claim was New Zealander Ernest Rutherford who had mentored Bohr while the latter had spent a postdoctoral year in England.

The cause of the partisanship is not so difficult to understand. The early 1920s were the years immediately following the Great War, and the victors, France and Britain, still resented German scientists and continued to prevent them from attending scientific meetings. In addition, the debate was taking place at a time when the French-Belgian alliance had occupied the Ruhr district of Germany. The Danes were, of course, not Germans, but they were regarded as guilty by association, both through geographical proximity and the fact that Denmark had remained neutral during the war. Ironically, neither discoverer of hafnium—neither Coster nor Hevesy—was German or even Danish. Nevertheless, they were treated as the enemy because the discovery was made in Denmark.[19] An example of the nationalism displayed by some parties can be seen in the following passage:

> We adhere to the original word celtium given to it by Urbain as a representative of the great French nation which was loyal to us throughout the war. We do not accept the name which was given it by the Danes who only pocketed the spoils of war.[20]

In the middle of this affair, Rutherford felt compelled to write to Bohr to say,

> We need pay no attention to such irresponsible utterances. . . . I will see you and your people get a square deal.

A more serious challenge to Coster and Hevesy came, a little later, again from Urbain and Dauvillier. They claimed, rather robustly, that Coster and Hevesy's work should be regarded as a detection of their own rare earth element, celtium, in zirconium minerals rather than as a discovery of a new element. Coster and Hevesy responded that hafnium could not be the same as Urbain's celtium because their own sample's X-ray lines suggested an element content of about 0.01%. Meanwhile, the elemental content of Urbain's samples would have had to have been considerably higher since he had claimed that he could detect a gradual change in magnetic susceptibility. In addition, Coster and Hevesy argued that subsequent analyses of the chemical properties of their hafnium showed similarities with the transition element zirconium and not to rare earth elements as Urbain had assumed celtium to be. Finally, Coster and Hevesy's colleagues in Copenhagen observed the optical spectrum of hafnium and found it markedly different from the one that Urbain had originally reported for his celtium.[21] Faced with this evidence, as well as a newly obtained optical spectrum of the element, Urbain was forced to admit that his original claim from 1911 was not justified and that his "celtium spectrum" had been due to element 71.[22]

Element 75—Rhenium

The existence of the element rhenium was predicted by Mendeleev when he first proposed his periodic table in 1869. It lies below manganese in group 7 of the short-form periodic table, which at the time was a unique group in having only one known element, manganese, as well as at least two gaps below it. The first gap was eventually filled by element 43, technetium, while the second gap would be filled by rhenium. Of these two elements, rhenium was the first to be discovered, in the year 1925, by Walter Noddack and Ida Tacke (later Noddack) (figure 11.9) and Otto Berg in Germany.[23] In the course of a heroically long extraction, they obtained just one gram of rhenium after processing about 660 kg of the ore molybdenite.[24]

The German discoverers called their element "rhenium" after Rhenus, the Latin for the river Rhine, which flowed close to the place where they were working. They also believed that they had isolated the other element missing from group 7[25], or element 43, although this was hotly disputed by several other researchers. As recently as the early years of the twenty-first century, research teams from Belgium and the United States reanalyzed the X-ray evidence from the Noddacks and argued that they *had* in fact isolated element 43.[26] But these further claims have been disputed by others and have now been laid to rest, at least for the time being.[27]

By a further odd twist of fate, the Japanese chemist Masataka Ogawa believed that he had isolated element 43 and called it nipponium even earlier, in 1908. His claim, too, was discredited at the time but as recently as 2004 was being championed again by the Japanese chemist Kenji Yoshihara.[28]

FIGURE 11.9
Ida Noddack (nee Tacke). Image by permission of Emilio Segrè. Collection at the Institute of Physics.

Noddack, Tacke, and Berg

In 1925 Noddack, Tacke, and Berg, working in Germany, reported that they had discovered two new elements in group 7, which they named masurium and rhenium, respectively. By an odd twist of fate, their claim for rhenium was upheld, whereas that for technetium was not. In fact, element 43 was only isolated, or rather synthesized, by Carlo Perrier and Emilio Segrè in 1937.

The Noddacks went beyond their competitors because they realized that the two elements they were seeking were not like manganese but more akin to their horizontal partners. For example, whereas manganese disulphide is soluble in acids, the Noddacks believed that elements 43 and 75 would be insoluble. They began by eliminating iron and manganese from their crude ores by the precipitation and filtration of these two metals. This involved making a total of 400 enriched products from different ores. In order to confirm the identity of the new elements, they enlisted the help of Otto Berg, an X-ray specialist at the Siemens-Halske Company in Berlin. In June 1925, the Noddacks along with Berg announced that they had identified a new element, and they proposed to call it rhenium, from a Norwegian columbite ore.

With the aid of a 30,000 Reichsmark grant from the German Scientific Energy Fund, the Noddacks traveled to Scandinavia and Russia to purchase further minerals they believed might contain rhenium. Their first success came in 1927 when they obtained 120 mg of rhenium and studied some of its chemical properties. There was commercial interest in the new metal almost immediately. Siemens and Haske, where Berg worked, then contracted the Noddacks to extract 1 gram of rhenium. This contract required that the extracted metal would become the property of the company, while still allowing the Noddacks to conduct further experiments on the metal. By 1929, the Noddacks duly delivered a whole gram of rhenium following the extraction from 660 kg of Norwegian molybdenite and reached a mass of 3 grams after one more year.

Further analysis showed that rhenium is present in the earth's crust at a very low concentration of 10^{-7}%, or 0.01 p.p.m. Although it does not form its own particular minerals, rhenium occurs in molybdenite, as has already been mentioned, as well as in porphyry copper ores. The metal has a melting point of 3180°C, making it only second to tungsten, which melts at 3380°C. The specific gravity of rhenium is the fourth highest of any element following Os, Ir, and Pt.

By 1925, all but one of the elements that occur naturally had been discovered. Just four gaps between the old limits of the periodic table remained to be filled. Although there were numerous claims for these missing elements, which were given fanciful names including masurium, illinium, florentium, alabamine, virginium, moldavium, russium, and a host of others, none of these claims have stood the test of time. It is also clear that none of these claims could possibly have been correct, given the highly unstable nature of the elements and the fact that, with the exception of francium, they had to be synthesized rather than discovered among naturally occurring sources.

The last four remaining elements—eventually named technetium, astatine, francium, and promethium—therefore form a separate, though not too well-defined, subclass among the last seven infra-uranium elements. They can also be regarded as forming a separate group of elements in view of the relatively long time delay before they began to be discovered. From the time of the discovery of hafnium in 1925, it was another 12 years before the next element was eventually synthesized in 1937. It took a further 10 years, however, before the name technetium, suggested by its discoverers, became accepted.

Element 43—Technetium

Element 43 holds a special distinction among the seven infra-uranium elements. It was one of just four elements that Mendeleev first predicted in his famous table and article of 1871. This fact is not so well known, as most accounts mention just the three famous predictions, namely, empty spaces to which Mendeleev gave atomic weights of 44, 68, and 72. These three elements were all discovered within a period of 15 years and were named scandium, gallium, and germanium, respectively (chapter 5). But in the same early table, Mendeleev assigned an atomic weight to just one more empty space, which he placed below manganese. Mendeleev also predicted that it would have an atomic weight of 100, although he changed it to 99 in his book, *The Principles of Chemistry*.[29]

Given the success of Mendeleev's first three predictions, it is hardly surprising that strenuous efforts were made, in many parts of the world, to find the fourth element. Little did these early chemists know the problems they would encounter in trying to isolate this particularly rare and unstable element. In the early twentieth century, several claims were made for its discovery. But these alleged elements, given various names such as davyum, illenium, lucium, and nipponium, all turned out to be spurious. Then, in 1925, as mentioned earlier, Otto Berg, Walter Noddack, and Ida Tacke (later Ida Noddack), claimed to have discovered not just one but two new members of group 7, which they named masurium and rhenium.

The official discovery of element 43 is accorded to Emilio Segrè and coworkers working in Palermo, Sicily. Technetium, as they eventually called it, had to be synthesized rather than isolated from naturally occurring sources. Segrè, who had been a visitor at the Berkeley cyclotron facility in California, was sent some molybdenum plates that had been irradiated for several months with a deuterium beam. Various chemical analyses by the Italian team revealed a new element, which could be extracted by boiling with sodium hydroxide that also contained a small amount of hydrogen peroxide.

It is generally believed that any technetium that might have been present when the earth was first formed has long since decayed radioactively. This is because even the longest-lived isotope of the element has a half-life that is too short in comparison with the age of the earth. However, in 1956, the Japanese radiochemist Paul Kuroda predicted that a natural nuclear reactor might once have existed deep within the Earth.[30] Five years later, he reported that a sample of African pitchblende contained about 2×10^{-10} grams of ^{99}Tc per kilogram of ore. In 1962, a team of French scientists confirmed Kuroda's earlier prediction of a natural nuclear reactor on investigating rock samples in the Republic of Gabon in Africa.[31] Further analyses showed that trace amounts of technetium were present in these minerals too, thus contradicting the common textbook statement that technetium does not occur naturally on earth.

The Claimed Discovery of Masurium

As already mentioned, Walter Noddack and Ida Tacke (who were later married), in an article published in 1925, made an extensive claim for having found not just element 43 but also element 75. This claim would continue to have repercussions right up to the twenty-first century, when attempts were made to rehabilitate the work of the Noddacks. Actually, they had succeeded in discovering only one of the two elements, namely, element 75, which they named rhenium. Their claim for element 43, which they called masurium and which entered the literature and appeared in periodic tables in some countries, has not survived for the simple reason that the discovery of this element had to await its artificial synthesis following the discovery of nuclear fission.

It is interesting to examine the article written by the Noddacks in order to glean something of their methodology. First of all, they made a number of statements about the relative occurrence of the elements in the central portion of the periodic table and recognized that the missing two elements in the manganese group would not necessarily resemble manganese, or at least that they would be more similar to the elements that flank them in a horizontal direction in the periodic table. The authors then presented a periodic table (figure 11.10) giving estimates of the abundances of many elements. The conclusion is once again that one should not expect to find eka-manganese and dwi-manganese in the ores of manganese, whereas they are more likely to be found in ores of molybdenum and ruthenium (for element 43) and tungsten and osmium (for element 75).

The Noddacks caused a great deal of resentment by choosing to call element 43 masurium. This name was an unfortunate blunder: apparently, it commemorated the crushing defeat inflicted on the Russians by the Germans in the Masurian district during the Great War of 1914–1918, thus perpetuating an incident of racial hatred.[32] If this were not enough, the Noddacks remained in their academic positions during the Nazi regime in World War II, which contributed to hostility toward their scientific claims to having discovered masurium.

Van Assche's Attempt to Rehabilitate the Noddack-Berg Claim for Element 43

The Belgian physicist Pieter van Assche published an article in 1988 in which he claimed to have rehabilitated the work of the Noddacks on the element they called masurium.[33] Van Assche began by pointing out that Ida Noddack had correctly predicted the possibility of nuclear fission some five years before it was actually discovered. The author then moved on to analyze three kinds of arguments.

Van Assche referred to the first argument as a credibility test. He accepted that if any element 43 was present in the ores that the Noddacks and Berg examined, then it must have been formed by the spontaneous fission of uranium. Van Assche therefore tried to establish a correlation between the ores that the Noddacks experimented upon and their uranium content according to present estimates. Van Assche argued that this approach lent good support to the original Noddacks-Berg claim since they reported that they had found element 43 in columbite, gadolinite, fergussonite, and sperrylite—all of which do indeed contain uranium, with the possible exception of sperrylite, for which current analyses are inconclusive. On

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
2.10^{-3}	3.10^{-5}	3.10^{-5}	7.10^{-2}	10^{-2}	3.10^{-6}	3.10^{-5}	10^{-7}	10^{-6}	10^{-9}	10^{-7}		
Y	Zr	Nb	Mo	**43**	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
1.10^{-6}	6.10^{-5}	10^{-7}	10^{-7}	$\approx 10^{-13}$	2.10^{-12}	10^{-11}	10^{-11}	10^{-9}	10^{-8}	10^{-9}	7.10^{-6}	7.10^{-8}
La	Hf	Ta	W	**75**	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
6.10^{-7}	6.10^{-6}	5.10^{-7}	5.10^{-7}	$\approx 10^{-12}$	2.10^{-11}	2.10^{-11}	10^{-9}	10^{-9}	10^{-9}	4.10^{-9}	4.10^{-7}	10^{-9}
	Th		U									
	7.10^{-8}		7.10^{-8}									

FIGURE 11.10 Relative abundance of the elements in the earth's crust as reported by W. Noddack and I. Tacke in 1925, including estimates for elements 43 and 75. Noddack, W., Tacke, I., Berg, O. Die Ekamangane *Naturwissenschaften*, 13 (26): 567–574, 1925.

the other hand, van Assche pointed out, the Noddacks and Berg claimed that they did not find element 43 in platinore, tantalite, or wolframite, and indeed these ores do not contain uranium according to current knowledge.[34]

The second of van Assche's arguments concerns the actual X-ray spectrum in which the Noddacks and Berg claimed to have observed evidence for element 43. First, van Assche mentions that the Noddacks calculated their experiment to have a detection limit of 10^{-9}, whereas he recalculated their detection limit to have been far lower—more like 10^{-12}. Van Assche also republished an image of the X-ray spectrum in which the Noddacks claimed to have detected some lines that could be attributed to element 43. The author asserted that the three reported lines labeled $K_{\alpha 1}$, $K_{\alpha 2,}$ and $K_{\beta 1}$ are extremely close to the values expected according to calculations, as are their relative intensities of 100:53:26, respectively.

Next, van Assche gave an estimate of the abundance of element 43 expected on the basis of its formation from the spontaneous fission of uranium. By using the value of the half-life of ^{99}Tc (2.1×10^5 years), the half-life of ^{238}U (6×10^{15} years), and assuming that the Noddacks's sample of columbite contained about 5% of uranium, van Assche arrived at a figure of about 10^{-13} for the abundance of element 43. This value is just one order of magnitude lower than the corrected detection limit that van Assche had calculated, namely, 10^{-12} as mentioned above. Van Assche concluded that the Noddack's experiments were easily capable of detecting element 43, since only one order of magnitude would seem to separate the detection limit of their X-ray experiment from the natural abundance of the element produced by the fission of uranium. Van Assche concluded that at least one of the ores, discussed in detail by Noddack, Tacke, and Berg, in their search for element 43, had a relative atomic abundance in the order of 10^{-13}. Van Assche concluded his article by affirming the priority of the Noddacks and Berg, and even suggested that the element should once again be referred to as masurium, the controversial name proposed by the Noddacks.

This article did not remain unchallenged for long. In the very next year, Gunter Herrmann of the University of Mainz in Germany (no nationalism was operating here) refuted all of van Assche's claims in great detail. On the "credibility argument" concerning the absence or not of uranium in the ores examined by the Noddacks, Herrmann pointed out that van Assche had failed to comment on a further 13 ores that were examined by the Noddacks and in which no element 43 was reported. Herrmann also mentioned that the Noddacks reported a uranium content of several percent not only in columbite but also in tantalite, in which element 43 was not claimed to occur. Herrmann pointed out that Tacke later listed a total of 27 minerals that he and the Noddacks had examined, whereas van Assche based his credibility argument on just six or seven ores.

On the question of the X-ray image, Herrmann pointed to some discrepancies, such as the fact that the distances between the assigned three lines were equal in the X-ray image, whereas in a grain-sized graph published alongside the spectrum the distances increased by factors of 1:2:3. Herrmann also reminded his readers that the story surrounding the X-ray plate was somewhat mysterious. For example, when Segrè asked to see the plate in 1937, he was told that it had been destroyed. Herrmann concluded by saying that he saw no argument for a revision of the history of element 43 in favor of an early discovery by Noddack, Tacke, and Berg.

Van Assche did not accept Herrmann's refutation. A few years later he approached the US geochemist John Armstrong, who was working at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, and asked for his help in analyzing the alleged X-ray spectrum of element 43. Not only did Armstrong support van Assche, but he undertook the task of simulating the X-ray spectrum of element 43 according to van Assche's calculations on the uranium content of the Noddack samples from 1925.

The outcome of this collaboration was two published articles, although neither appeared in the primary research literature. The first was an anonymously authored note of less than one page in the November–December 1999 issue of the NIST journal.[35] The note began by repeating the fact that the claimed discovery of element 43 by the Noddacks and Berg had been invariably derided and dismissed. The other published item was an entry in the otherwise excellent compilation of articles commissioned by the US magazine *Chemical & Engineering News* in a special issue commemorating the 80th anniversary of the publication.[36]

Nothing was heard again on this debate until an article was published in the *Journal of Chemical Education* in 2005.[37] There, an Italian author, Roberto Zingales, gave a history of the discovery of element 43 and attempted to support Armstrong's claim. A response followed immediately. Fathi Habashi, a professor of metallurgy from Laval University in Quebec, Canada, sent a letter to the editor pointing out that the claim by van Assche and Armstrong "cannot stand up to the well-documented assertion of the well-established physicist Paul Kuroda (1917–2001) in his paper 'A Note on the Discovery of Technetium.'"[38] He was referring to Kuroda's work on the amount of uranium present.

The same issue of *Journal of Chemical Education* of 2005 also carried a full retraction by Zingales in which he mentioned the objections of Habashi and Hermann and the fact that he now realized that the claims of van Assche and Armstrong could not be sustained.[39]

Finally, the "Real" Element 43 Is Obtained

Following all the failed attempts to isolate element 43, including that of the Noddacks and Berg, the element was finally and genuinely obtained in 1937. It was a product of a synthetic process rather than a case of isolation from naturally occurring minerals. It was also the first time that an element was discovered following its artificial synthesis.

Although very small amounts of element 43 were subsequently found to exist naturally, the first discovery of the element was carried out using a plate of molybdenum metal that had been irradiated with deuterons and neutrons. Unlike the synthetic elements that are created these days, the discovery of element 43 was somewhat serendipitous in that it did not follow a deliberate attempt to create the element. Instead, the researchers happened to find it while analyzing a sample that had undergone irradiation such as to bring about the transmutation of one element, molybdenum, number 42, to the following element, number 43. This is not to say that the physicists and chemists concerned were completely oblivious to the possibility of the presence of element 43. Rather, they quickly suspected that it might be present from knowledge of radioactive processes, and so they set about trying to detect the possible existence of element 43.

The task fell to Italian physicist Emilio Segrè, who had spent a postdoctoral fellowship at the Berkeley lab of Ernest Lawrence, the creator of the cyclotron machine. Segrè then returned to his permanent job in Palermo, Sicily, and was sent an irradiated sample of molybdenum by a fellow countryman who was still in California. Together with the chemist Carlo Perrier, Segrè undertook the task of eliminating all other possible elements, given that many others were also produced in the original irradiation.

Segrè and Perrier succeeded in isolating the isotopes technetium-95 and technetium-97. In 1940, Segrè and Chien-Shiung Wu also found element 43 to be a product of the fission of uranium. The University of Palermo officials wanted them to name their discovery panormium, after the Latin name Panormus for Palermo. But element 43 was named after the Greek word τεχνητός, in 1947, meaning "artificial," since it was the first element to be artificially produced. In doing this, the authors were following the suggestion by Friedrich Paneth, who wrote in the same issue of *Nature* magazine as Segrè and Perrier.[40] It is worth considering Paneth's paper since it reveals a hidden aspect of the story of a number of the seven elements discussed in this chapter (figure 11.11). The simple fact is that for many years chemists did not consider the artificially synthesized elements to be true elements. In many cases, the newly discovered elements remained nameless and did not appear on the periodic table. There was a general feeling in some circles that synthetic elements were somehow quite different from naturally occurring ones. The initiative to change this situation was taken by Paneth.

Paneth suggested that whereas the denial of "full citizenship" to artificial elements may have been justified in his 1942 lecture, this was no longer the case in 1947. In 1942, the elements that had been produced artificially were all unstable, had only been produced in invisible amounts, and were not present on the earth. In the intervening five years, several pounds of one particular element, plutonium, number 94, had been stockpiled. Moreover, its half-life of some 200,000 years ensured that plutonium would remain on earth for many years to come! Finally, the developing technology made it clear that many more elements, with even

Periodic Classification of the Chemical Elements

Period	Group																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I																	1 H 1.0080	2 He 4.003
II	3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.0000	9 F 19.00	10 Ne 20.183
III	11 Na 22.997	12 Mg 24.32											13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
IV	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
V	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43—	44 Ru 107.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 X 131.3
VI	55 Cs 132.91	56 Ba 137.36	57-71 Rare Earths†	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 192.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210	85—	86 Rn 222
VII	87 AcK 223	88 Ra 226.05	89 Ac 227	90 Th 232.12	91 Pa 231	92 U 238.07	93—											

† Rare Earths

VI 57-71	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61—	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tu 169.4	70 Yb 173.04	71 Lu 174.99

FIGURE 11.11 From Paneth's article of 1942. F.A. Paneth, Radioactivity and the completion of the Periodic System, *Nature*, 149, 565-568, 1942. Reprinted with permission from Nature Publishing Group.

higher atomic numbers, could soon be produced. Paneth wrote that the time had come for the systematizing chemist to no longer discriminate between natural and artificial elements, but to pay equal attention to study of both and to insert the appropriate symbols into the periodic table. Paneth suggested the following set of rules for assigning names and symbols for elements 43, 61, 85, 87, 93, 94, 95, and 96.

1. The right to name an element should go to the first to give definitive proof of the existence of one of its isotopes.
2. In deciding the priority of the discovery, there should be no discrimination between naturally occurring and artificially produced isotopes.
3. If a claim to such a discovery has been accepted in the past, but refuted in later research, the name given should be deleted and replaced by one chosen by the real discoverer.

At this point, Paneth launched into something of a tirade against the Noddacks in particular. He lamented the failure of claimants to withdraw their statements, even though many years of intensive efforts had failed to support their claims. He further mentioned that during the war, when Noddack was appointed professor of inorganic chemistry by the occupying powers in Strasbourg, the symbol Ma continued to occupy the space for element 43 on the periodic table of the chemistry lecture hall. After making it clear that he believed Segrè and Perrier were the discoverers of element 43, and similarly emphasizing the true discoverers of elements 61, 85, and 93, Paneth concluded his article with the following invitation to his colleagues,

> So far no names for elements 43, 61 and 85 have officially been put forward by their discoverers, Perrier and Segrè, Coryell and his group, and Corson, MacKenzie and Segrè respectively. Every chemist concerned with the task of teaching systematic inorganic chemistry and of keeping his table of the Periodic System up to date will be grateful if they will publish soon the names which they consider suitable.

The editor of *Nature* magazine appears to have acted immediately since in the very same issue two of these three teams published letters in which they officially unveiled their proposed names and referred to Paneth's article in doing so.[41] Segrè later returned to Berkeley and met Glenn T. Seaborg. There at Berkeley, in 1938, they had isolated the metastable isotope technetium-99m, which is now used in millions of medical diagnostic procedures throughout the world.[42]

The Oklo Phenomenon

In 1939, at a time when the study of nuclear reactions was still in its infancy, Siegfried Flügge published an article in which he speculated about the possibility of a self-sustaining chain reaction involving the element uranium that might have taken place under natural conditions in the past.[43] Flügge also suggested that such an event might have taken place in the large uranium deposit in St. Joachimstahl, Bohemia, or alternatively in the carnotite deposits in the US state of Colorado.

Meanwhile, the first *human-made* sustained nuclear reactor was built at the University of Chicago in 1942 by the Italian-born physicist Enrico Fermi. The success of Fermi's achievement, and the scientific and engineering demands of this work, was interpreted by many physicists to mean that any such natural process would not have been possible. Nevertheless, very strong evidence of such a natural process was discovered in the 1970s, by the French Commissariat a l'energie atomique (CEA) working in the African republic of Gabon. Even more remarkably perhaps, the age of such a pre-Fermi reactor, as it became known, was predicted with amazing accuracy in 1965 by Japanese nuclear chemist Paul Kuroda, working at the University of Arkansas. By making a few basic assumptions, Kuroda reached the conclusion that the natural reactor would have been active about 2×10^9 years ago. Following the French discovery of the Oklo reactor in the Gabon, the calculated age of the event was placed at precisely 2×10^9 years ago, in agreement with Kuroda's prediction. The reaction of the physics community was one of complete surprise.

The Oklo reactor was discovered in June 1972 as a result of a significant anomaly in the ratio of the two main isotopes of uranium, namely, ^{235}U and ^{238}U. Whereas the normal fraction of ^{235}U in naturally occurring uranium is 0.7202% +/– 0.0010%, the minerals from Oklo were found to contain 0.440% of the same isotope. The conclusion arrived at by the French nuclear scientists was that a self-sustaining nuclear chain reaction had taken place at the time that Kuroda had predicted. Estimates of how long the natural nuclear reactor had existed varied between 600,000 and 1.5 million years. In addition, it was deduced that the presence of oxygen in the atmosphere had participated in the fractionation processes occurring within the uranium minerals. This also coincided with the independent estimates that the earth's atmosphere underwent a dramatic enrichment in oxygen 2×10^9 years ago as a result of the generation of new living organisms capable of the process of photosynthesis.

Further analysis of the minerals in the Oklo reactor showed that a number of elements that had previously been thought to be absent from the earth did in fact occur as a result of such unusual nuclear phenomena. These elements included technetium, promethium, and even element 93, or plutonium.[44]

Element 87—Francium

The discovery of element 87 has been claimed by a number of scientists following its prediction by Mendeleev in 1871, who gave it the provisional name of eka-caesium.

(It was recognized early on that the periodic table more or less ends out after element 83, or bismuth. All subsequent elements are radioactive and therefore unstable, with a few exceptions like uranium and thorium. But this fact did not deter a number of scientists from searching for element 87 among natural sources and in many cases from claiming to have isolated it. For example, Gerald Druce and Frederick Loring in England thought they had identified the element by using the classic method developed by Moseley for measuring the K_α and K_β lines of any element's X-ray spectrum. But it was not to be.

In the 1930s, Fred Allison from the Alabama Polytechnic Institute (now Auburn University) developed what he called a magneto-optical method for detecting elements and compounds. This method was based on a supposed time lag in the development of the Faraday effect, whereby the application of a magnetic field causes a beam of polarized light passing through a liquid solution to be rotated. Allison mistakenly thought that every element gave a particular time lag, which, he claimed, could be observed with the naked eye, and that this could be used to identify each substance. He boldly claimed in a number of journal articles and a special feature in *Time* magazine that he had observed elements 87 and also 85, both of which were still missing at the time. Dozens of papers were published on this effect, including a number of studies arguing that it was spurious. These days the Allison effect is often featured in accounts of pathological science, alongside the claims for N-rays and cold fusion.[45]

The next major claim came from Paris and was supported by Jean Perrin, the physicist best known for having corroborated Einstein's theory of Brownian motion and for providing supporting evidence for the real existence of atoms. Horia Hulubei, a Romanian physicist working with Perrin, claimed to have used highly accurate X-ray measurements and to have recorded several spectral lines with precisely the frequencies expected of element 87, which he promptly named moldavium. But these lines also turned out to be spurious.

The eventual discovery of element 87 was made by a Frenchwoman, Marguerite Perey, who began life as a laboratory assistant to Marie Curie in Paris. Perey became skillful in purifying and manipulating radioactive substances and was asked to examine the radioactivity of actinium, or element number 89 in the periodic table. By carefully excluding all daughter isotopes, she was the first to observe the α and β radiation produced by actinium itself rather than its radioactive daughter isotopes. She thereby discovered a weak but significant branch in one of the three main radioactive decay series. Her analysis of the data revealed a new element with a half-life of 21 minutes. When asked to name the element, she chose francium to honor the country of her birth.[46] It was also an appropriate choice to mark the continuing contribution of French scientists to the study of radioactivity. The phenomenon was first discovered by Becquerel, the Curies isolated polonium and radium, and Debièrne isolated actinium, all within a few years of each other and all in France.

As it turns out, francium was the last natural element to be discovered. Estimates of the abundance of francium suggest that there is only about 30 grams in the whole of the earth's crust. It is one of the very few elements that has no commercial applications, mainly because its longest-lived isotope has a half-life of just 21 minutes. Nevertheless, the fact that the francium atom has the largest diameter of any element, at an outstanding 2.7 Ångstroms, and the fact that it has just one outer-shell electron, have made it the object of considerable attention among researchers wanting to probe the finer details of current theories of atomic physics. In 2002, a group in the United States succeeded in trapping 300,000 atoms of francium and in performing several key experiments of this kind.[47]

Francium

In 1939, element 87, or eka-caesium, was truly discovered by an unknown French laboratory technician, Marguerite Perey, although she was no ordinary technician. She had the good fortune to become the personal assistant to Marie Curie and to be trained by her in the manipulation of radioisotopes. Eventually, she would earn a degree, followed by a PhD and rise to the rank of professor of nuclear chemistry. It was in her PhD thesis where she reported the crucial experiments that show conclusively her discovery of the long-sought eka-caesium.

In retrospect, it is not difficult to see why earlier attempts did not amount to much, since all elements beyond atomic number 83, or bismuth, are radioactive, whereas previous attempts had mostly been conducted in nonradioactive minerals. At the time of Perey's work, several radioactive elements had been discovered in the previous 15 years, mainly in France. They were polonium (84), radium (88), actinium (89), and protactinium (91). Any researcher hoping to discover element 87 had to be working in the field of radiochemistry if they stood any chance of being successful.

But even within radiochemical research, there were a number of individuals who came close to discovering element 87, and again it is easier to understand why this was so in retrospect. In 1913, it was known that there were three main radioactive decay series that began with radium, thorium, and actinium. In addition, the radioactive displacement laws were already known, whereby the emission of α radiation resulted in the formation of an isotope with an atomic number of two units less than the decaying isotope, while β emission produced an isotope with one unit of atomic number higher.

Consequently, from the early days of radiochemistry, it was apparent that element 87 would probably be formed from either the α decay of actinium (88) or the β decay of radon (86).

$$_{89}\mathrm{Ac} \rightarrow {}_{87}\text{eka-Cs} + {}_{2}\alpha$$
$$_{88}\mathrm{Rn} \rightarrow {}_{87}\text{eka-Cs} + {}_{-1}\beta$$

However, the known isotopes of actinium appeared to be just β emitters, while those of actinium were only α emitters. Nevertheless, the possibility of an isotope decaying via both forms of decay was recognized. Eventually, eka-cesium was found as the result of the dual α and β decay of actinium, and so we need to turn briefly to the history of that particular element.

Actinium was discovered in 1900 by André Debièrne, who was a colleague of the Curies in Paris. He called it actinium from the Greek ακτινοσ, or "ray," even though the observable radiation from this element is almost negligible. In 1908 Otto Hahn, then working at University College London, discovered what was first believed to be a new element, which was provisionally named mesothorium-2, or MsTh2. In fact, he had discovered another isotope of actinium, ^{228}Ac, in addition to Debièrne's ^{227}Ac.

As a result, there were now two candidate isotopes of actinium that might be the source of eka-cesium, although nobody pursued these possibilities or tried to detect whether they were actually α emitters. It was only in 1926 that Hahn decided to actively search for eka-Cs from his ^{228}Ac, but he failed to see any α decay. He realized that a similar search should be carried out with the other isotope, ^{227}Ac, but as he later claimed, he had lacked the skills required to purify actinium. These were exactly the skills that Perey possessed and was able to utilize in her eventual discovery of the new element.

Another group of radiochemists who missed the discovery of eka-cesium were Stefan Meyer, Victor Francis Hess, and Paneth in Vienna. While conducting a survey of emissions from a number of isotopes, they noticed that ^{227}Ac might indeed be an α emitter of very small intensity and reasoned that the radioactive decay series involving actinium might still be lacking some unknown elements. However, this work was brought to an abrupt end by the outbreak of World War I.

As George B. Kauffman and Jean-Pierre Adloff have claimed, the Vienna team had probably measured the direct α emission from ^{227}Ac but without being sure of it.[48] Had they known that this was the case, they would have claimed the discovery of the new element. As mentioned earlier, the radioactive decay laws unequivocally imply that the emission of α radiation from actinium (89) produces an element with an atomic number of two units lower, namely, element 87, or eka-Cs. But as late as the early 1930s, Marie Curie wrote that actinium does not emit any observable radiation.

Perey

Marguerite Perey joined Curie's laboratory, l'Institut du Radium, in 1929. From the beginning of her work, Curie trained her in working with actinium, including concentrating the element when it was present in a mixture of rare earths that frequently included lanthanum. This task required repeated crystallizations and evaporations of compounds such as the oxalates of the metals. Manipulations with actinium also required working quickly because this radioactive series produces isotopes of thorium, radium, lead, bismuth, and thallium in quick succession. If actinium was to be studied for its own properties, all these daughter isotopes had to be quickly removed, especially as they produced their own α and β radiations.

Although Marie Curie died in 1934, Perey pursued the work on actinium, now under the joint direction of the discoverer of the element, Debièrne, and also Irène Joliot-Curie, Marie Curie's daughter. Both of Perey's new mentors encouraged her to continue to purify and examine the radioactive properties of actinium. By now it was clear that ^{227}Ac had to be a β emitter since one of the daughter isotopes was ^{277}Th.[49] Nevertheless, nobody had directly observed this β emission from actinium itself.

In 1935, Willard Frank Libby and Wendell Latimer, in the United States, thought they had detected such radiation. Perey's interest was aroused by this report, as she suspected that it was probably due to some of the daughter isotopes. She was thus motivated to mount her own search for β radiation coming directly from actinium. The work required that she concentrate a source of actinium and begin to look for its radiation about one minute later, before it became swamped by that of its daughter isotopes.

While carrying out these procedures, Perey discovered that during the first two hours the radioactivity increased rapidly, reaching a plateau, and then increased again slowly. By extrapolating her graph to a time of zero, she succeeded in obtaining a numerical estimate for the α and β radiation from pure actinium. It turned out that about 1% of the radioactivity was α decay and the remaining 99% was in the form of β decay. Perhaps the most crucial part of the observation was that the initial radioactive decay of actinium took place with a half-life of 21 minutes, a fact that she recorded on January 7, 1939, in a notebook, which survives to this day.

Gathering this information together, Perey deduced that the decay of ^{227}Ac occurs mainly through the formation of thorium, radium, and other daughter products, but that there is also a small, almost insignificant branching detour that would mean either the presence of a new element or possibly the existence of a yet unrecognized further isotope of actinium. Perey was confident that the α decay could not be attributed to daughter isotopes like thorium and radium, and so it had to be due to actinium itself. This meant that actinium might be decaying into element 87, given that α decay results in a lowering of the atomic number by two units.

The rapid increase in β decay that Perey observed was not therefore due to actinium itself but perhaps due to the decay of element 87 into ^{88}Ra. Of course, actinium itself shows β decay. In fact, 99% of its activity is due to this form of decay, as noted above. But since this process has a much longer half-life, it could be distinguished from the β decay of element 87. The chemical identity of the new element was confirmed by the fact that it could be precipitated with caesium salts. Caesium is an alkali metal in group 1 of the periodic table, as eka-caesium was expected to be since the time of Mendeleev's original prediction of the element. But none of this information was completely conclusive, and there was still the question of whether a new isotope of actinium was giving rise to some of the observations on the decay of freshly prepared ^{227}Ac.

Perey showed considerable caution in announcing her discovery in a short article in the *Comptes Rendus de l'Académie des Sciences*. The paper was presented by Jean Perrin, who rather ironically believed that eka-caesium had been discovered earlier by one of his own collaborators, the Romanian physicist Horia Hulubei.[50] Perey initially named the new isotope actinium K, as she could not be certain of its precise identity.

During the course of this work, Perey had kept her two mentors, Debièrne and Joliot-Curie, separately informed of her progress. Eventually, Joliot-Curie happened to mention to Debièrne that Perey had discovered a new isotope or element as a result of her own suggestion. At this point, Debièrne is said to have fallen into a rage, having thought that he had been the sole director of Perey's work. A consequence of this dispute was that the two mentors could not agree as to which of them should share the credit with Perey, with the result that she was recognized as the sole discoverer.

When it became clear that Perey had discovered a new element rather than a new isotope of actinium, she was invited to name her new discovery by Paneth, the then head of the nomenclature commission of IUPAC. Perey suggested the name catium to mean cation, since the new element would form the largest cation in the periodic table. This idea was opposed by Irene Joliot-Curie, who felt that speakers of the English language would mock the name because it sounded too much like the household pet, "cat." Perey then settled for the name francium to honor France and suggested the symbol of Fa, although shortly afterward, the symbol was changed to Fr to be more in keeping with the manner in which other elements are symbolized.

Following Perey's discovery, both of her mentors encouraged her to obtain the degree she still lacked. Perey found herself in the remarkable situation of having enough material for a doctoral thesis and yet not possessing an undergraduate degree, which in turn meant that she could not even register for the doctoral process. Nevertheless, she quickly obtained various certificates in a number of subjects before finally defending her doctoral thesis in 1946. In 1949, she was appointed to a chair in nuclear chemistry at the University of Strasbourg. Meanwhile, she had begun to suffer from radiation sickness as a result of her work with radioactive isotopes, and eventually died prematurely at the age of 65 in 1975.

Perey had discovered the last naturally occurring element and all that remained were elements 61 and 85, which would require being artificially synthesized.[51]

Element 85—Astatine

The story surrounding element 85 is one of the most complex and interesting among the final seven infra-uranium elements. The various claims for its discovery reveal many of the nationalistic traits that we have seen in the case of other elements, most notably the controversy surrounding the discovery of hafnium, element 72.

But element 85 gives greater depth than has yet been revealed by the previously covered elements. What this story shows is that the nationalistic prejudices persist to this day in many respects and that the identity of the "discoverer" of the element very much depends on the nationality of the textbook that one might consult. It is also an element for which the majority of sources give an incorrect account in declaring Dale R. Corson, Kenneth Ross MacKenzie, and Emilio Segrè as the sole discoverers. The account I will follow owes much to the recent work of two chemists, Brett Thornton and Shawn Burdette, whose 2010 article I have drawn from.[52]

As in the case of many of the seven elements already surveyed, the view that Moseley's experimental demonstration of the concept of atomic number resolved all issues in a categorical fashion is once again shown to be misleading.

Early Claims for Element 85

The position of element 85 in the periodic table shows it to lie among the halogens. Not surprisingly, therefore, the early researchers believed that they would find the element in similar locations to other halogens such as bromine and iodine, namely, in the oceans or in sands washed up by oceans. Moreover, it was also expected that the new element would behave like a typical halogen to form diatomic molecules and that it would have a low boiling point.

The first major claim for the discovery of the element was made by Fred Allison, the same researcher who also erroneously claimed that he had discovered element 87. And just as in the case of element 87, Allison claimed to have found the new element using his own magneto-optical method, involving a time delay in the Faraday effect, which is to say the rotation of plane polarized light carried out by the application of a magnetic field to any particular solution of a substance. Allison published articles in 1931 and 1932 claiming that he had observed element 85 and proposing to call it alabamium after Alabama, the state in which he worked.

In 1935, the American physicist H. G. MacPherson showed that Allison's findings were spurious and due to imperfections in his instruments rather than to the presence of a new element.[53]

The next claim came from Rajendralal De, an Indian chemist working in Dacca, which was then part of British India and is now in Bangladesh. De had trained in Germany with Hahn and Meitner in the 1920s and like Allison, used monazite sand in his research. After applying a number of chemical processes, De obtained a sublimate that he claimed to be element 85 and to which he gave the name of dakin after the city of Dacca. Later researchers dismissed De's claim on the basis of the powerful radioactivity of astatine, which would have prevented him from safely handling the element in the manner he claimed to have done at the time.

Another person who had been involved in the search for element 87, Romanian Horia Hulubei, was also involved in the discovery of element 85. Indeed, it appears that he may well have been the discoverer of naturally occurring astatine, as it was later called by the physicists who synthesized the element artificially. Hulubei studied in France starting in 1916, returning to his native Romania at the end of World War I in 1918. In 1926, he came back to France to work with Jean Perrin and built an X-ray laboratory at the Sorbonne. In 1928, they were joined by Yvette Cauchois, who built what later became known as the Cauchois spectrometer, which provided higher-resolution spectra and made possible the study of weaker spectra than had previously been observed. Hulubei and Cauchois examined the radioactivity of radon in the hope of observing evidence of the presence of element 85.

In a paper published in 1936, Hulubei and Cauchois claimed to have observed a line at 151 X-units or siegbahns exactly where the $K\alpha 1$ line for eka-iodine was expected.[54] In 1939, they reported two further X-ray lines consistent with the presence of eka-iodine and the predictions from Moseley's law. These new experiments used higher resolutions and included further checks and balances, which led to greater confidence in the authors' claims to having discovered the new element. In 1941, a former student of Hulubei and Cauchois, Manuel Valadares, repeated the experiments with a stronger X-ray source after returning to his native Portugal. He subsequently published his results, and also supported the presence of eka-iodine.[55]

In 1942 two women, Berta Karlik and Traude Bernert, working at the Institute for Radium Research in Vienna, reported the detection of α particles from the radioactive decay of a radon isotope.[56] They took this decay to indicate the presence of element 85 in part of a natural radioactive decay series. By this time, the artificial synthesis of element 85, which is generally considered to be the definitive discovery of the element, had been conducted at Berkeley. The Austrian researchers were unaware of this fact, however, due to lack of communication during wartime.

In an article of 1944, Hulubei wrote a detailed summary of his work and that of others on element 85. This report included a description of six X-ray lines that were thought to be due to natural radioactive decay producing the new element. He also appealed to the work of Karlik as providing support for his own findings. This time Hulubei went as far as to suggest a name for the new element, dor, which he took from the Romanian word for "longing" in the sense of "longing for peace."

As World War II drew to a close and some elements began to be produced artificially, it became important to decide on how elements should be named and who would have the right to give them new names. This task was taken up by the Austrian-born radiochemist Friedrich Paneth, who had fled from Berlin to the United Kingdom in 1936 after being dismissed from his professorship due to his Jewish origins. Paneth published an editorial in *Nature* magazine in 1947, thereby prohibiting any discovery claims from Hulubei and Cauchois. Paneth suggested that in cases in which an element had been given different names by competing groups, the naming rights should go to those who produced the element in a reproducible fashion. This meant that, in the case of element 43, the Noddacks's claim for masurium should be dismissed and should be replaced by technetium, as synthesized by Segrè and Perrier.

Paneth noted the claim by the Berkeley group for the synthesis of element 85 and also the fact that Karlik and Bernert had shown that it exists in natural sources. But he went on to state that what he called "former claims," without naming any particular researchers, had been disproved by the work of Karlik and Bernert. This statement served to discredit the work of Hulubei and Cauchois, even though Karlik and Bernert had not actually addressed these claims, whereas Paneth's statement implied that they had.[57]

Hulubei was understandably very concerned with Paneth's editorial and the implication that his work and that of Cauchois had been refuted. He responded by attributing Paneth's omission to the difficulties in communication during the war. He denied that Karlik and Bernert had refuted his own research on element 85, ending with the words, "contrary to what one would think after reading the expose of Mr. Paneth." Soon afterward, Karlik finally did comment on Hulubei's work, claiming that the research had been insufficient to merit the discovery of element 85 because of the very small amount of element 85 in their sample, which would likely render some interference from other elements in the X-ray spectra.[58]

In a further response to Paneth's editorial, three Berkeley researchers claiming to have produced element 85 artificially—Corson, MacKenzie, and Segrè—proposed the name astatine from the Greek *astatos*, or unstable. The authors had not been aware of the claims from Hulubei and Karlik but had delayed proposing a name for the element because of the continuing claims for alabamine by Allison and his supporters. Paneth, who was by now the chair of the committee of the International Union of Chemistry, approved the name of astatine in 1949, thus further lending his support to the American claim.

According to the analysis of Thornton and Burdette, there is no doubt that three teams of researchers can claim to have discovered element 85.[59] First of all, they state that unlike the cases of other flawed studies with X-ray spectroscopy, Hulubei and Cauchois indisputably had element 85 in their samples and that the only uncertainty is whether their instrument was sensitive enough to distinguish the spectral lines of element 85.[60]

Hulubei and Cauchois have never received much credit for their work in part because of Paneth's disparaging words to the effect that "other work" on element

85 had been refuted, even though Hulubei and Cauchois's work had not. In addition, Thornton and Burdette attribute the lack of credit to the fact that Hulubei in particular had falsely claimed the discovery of element 87 and that he had definitely been wrong in that case. They propose that this earlier error caused others to doubt Hulubei, even though he had detected element 85.[61]

The Usually Acknowledged Discovery of Element 85

The discovery of element 85 was made by three Berkeley scientists, Dale Corson, Alexander MacKenzie, and Emilio Segrè, in 1940. Using a 60-inch cyclotron built by Ernest Lawrence, the three scientists bombarded a target of bismuth, element 83.[62] This element is useful in this context because it has just one single isotope, a feature that greatly simplifies the analysis of products. The bombarded bismuth target produced a number of forms of radiation, including α, γ, X-rays, and even low-energy electrons, all exhibiting the same lifetime of about seven-and-a-half hours. Through a series of analyses, the authors were able to identify the substance causing some of these radiations, with element 85, which was changing into polonium via K-electron capture.

$$^{211}_{85}\mathrm{At} + {}_{-1}\mathrm{e} \rightarrow {}^{211}_{84}\mathrm{Po} + 90 \text{ kilovolt X-ray}$$

In the article announcing their discovery, they also remarked about the possible existence of naturally occurring element 85 and cited the earlier work of Walter Minder in Switzerland, as well as Hulubei and Cauchois in Paris, both of whom had claimed to have observed the element.

Moreover, they cited the work carried out with Joseph Hamilton and Mayo Soley in which element 85 was concentrated into the thyroid glands of some guinea pigs, showing similar excretion to that of iodine, which occurs above element 85 in the periodic table. Nevertheless, the chemical experiments of Corson et al. revealed that the properties of element 85 are more similar to those of neighboring element 84 or polonium than they are to iodine. For example, element 85 precipitates as a sulfide and is precipitated by zinc in sulfuric acid, both of which are reactions that are characteristic of a metal rather than a nonmetal such as iodine.

Element 61—Promethium

The last of our seven elements to be isolated was element 61, which is also the only rare earth among the seven. The problem with rare earths, which are 15 or even 17 in number depending on precisely how they are counted, is that they are extremely similar to each other and as a result are very difficult to separate. When the periodic table was first created in the 1860s, only two or three rare earths even existed. As more of them turned up, it became increasingly difficult to place them in the periodic system.

Early Claims

As is the case for all the elements featured in this chapter, there were many false claims to the discovery of promethium. Moreover, the early claims must have seemed very plausible at the time because they drew support from X-ray evidence and Moseley's law. Just like the priority dispute involving hafnium that took place in the early 1920s, the case of element 61 also involved an international priority dispute. This time one cannot entirely blame the aftermath of the Great War, as the two opponents were Italian and American. Much of the scientific combat took place, as was usual for the time, in the pages of London's *Nature* magazine.

But even though both sides of the priority dispute appealed to X-ray data and Moseley's law, it turned out that neither side was correct. Each side was working in complete delusion, since element 61 is highly radioactive and unstable, does not occur naturally on earth, and could only be isolated in minute quantities by artificial means when such methods became sufficiently developed in the 1940s.

In 1902, the Bohemian[63] rare earth chemist Bohuslav Brauner was the first to suggest that an element lying precisely between neodymium and samarium remained to be discovered. He gave talks in his native country and published articles in some obscure journals, all of which meant that few chemists in the wider chemical arena became aware of his work. In 1927, during the height of the priority debate over element 61, in a letter to *Nature*, Brauner felt compelled to assert his priority regarding his 1902 prediction that such an element should even exist between neodymium and samarium (figure 11.12). This letter is also interesting because it again highlights the fact that Moseley's method was not quite as categorical as is often portrayed.

Beginning in the 1870s, Brauner worked on chemical substances that supported the validity of Mendeleev's periodic law (chapter 5). In 1881, he began a correspondence with Mendeleev, and a strong personal friendship developed between them. Among other things, Brauner demonstrated that beryllium in its compounds is bivalent and not trivalent, thus confirming the accuracy of Mendeleev's correction of the atomic weight of beryllium according to the periodic law. Brauner's studies on the rare earth elements and the determinations of their atomic weights were of particular importance, causing Mendeleev to remark that Brauner was one of the first chemists to confirm the conclusions from the periodic law. In 1900, Brauner proposed that the rare earth elements be placed in a distinctive "interperiodic" group immediately after lanthanum. His fundamental idea was eventually corroborated by discoveries in atomic structure. At Mendeleev's request, Brauner also wrote the section entitled "Rare-Earth Elements" for the seventh edition of Mendeleev's book *Osnovy khimii* or *The Principles of Chemistry.*

Das periodische System der Elemente.

Gruppen	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Reihen	(RX_7) R_2O	(RX_6) R_2O_2	(RX_5) R_2O_3	RH_4 R_2O_4	RH_3 R_2O_5	RH_2 R_2O_6	RH R_2O_7	$\left.\begin{matrix}(R_2H)\\(R_2O_8)\end{matrix}\right\}$ Verbindungsformen
1.	1 Li							
2.	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3.	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35.5 Cl	
4.	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 59, Cu 63
5.	(63 Cu)	65 Zn	69 Ga	72 ?	75 As	78 Se	80 Br	
6.	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	? 100	Ru 104, Rh 104, Pd 106, Ag 108
7.	(108 Ag)	112 Cd	114 In	118 Sn	120 Sb	126 Te	127 J	
8.	Cs 133	Ba 137	La 139	Ce 141.6	Di 146.7	Tb 148.8 ?	Sm 150 ?	? 152, ? 153, ? 154, ? 156
9.	156 ?	158 ?	? 159 Ya?	162 ?	166 Er?	167 ?	? 169 Tm?	
10.	? 170	? 172	Yb 173	? 177	Ta 182	W 184	? 190	Os 193 1), Jr 193, Pt 195, Au 197
11.	(197 An)	200 Hg	204 TI	207 Pb	210 Bi	? 214 Ng ?	219 ?	
12.	? 221	? 225	? 230	Th 234	? 237	U 240	? 244	

1) Aus der Dampfdichte des Os O4 (Deville und Debray, Ann. chim. phys. (3) 56, 476) ergiebt sich die Zahl 193 als Atomgewicht des Osmiums.

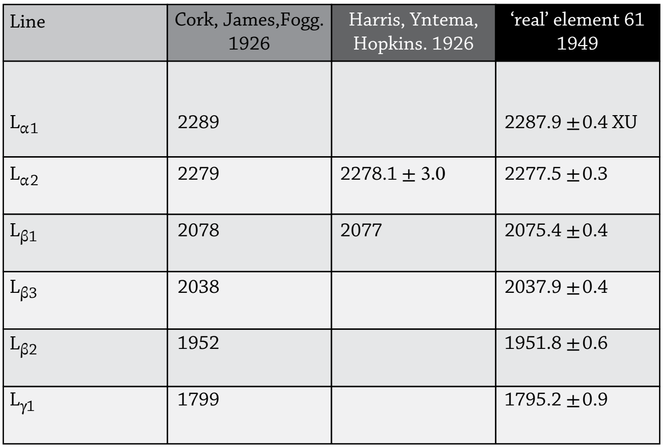
FIGURE 11.12 Brauner's periodic table of 1882 with a homologous accommodation of the rare earth elements. *Chemical News*, 58, 307: At this stage there is no hint of an element between Nd and Sm. In fact, Nd had not even been discovered.

In his 1927 letter to *Nature*, the 72-year-old Brauner began by congratulating the American researchers for their discovery of illinium, their name for element 61. He continued by drawing attention to the paper which claimed that there was no theoretical grounds for the proposition that eka-neodymium might exist until Moseley's rule could show that element number 61 was still to be identified. Brauner reminded readers that he had devoted almost all his scientific life to the study of the rare earth elements and their role in the periodic table of the elements. He commented on how he had arrived at the realization that the gap between the atomic weights of neodymium and samarium was abnormally large in amounting to 6.1 units of atomic weight. This value, as he wrote, was larger than that between any two elements in the periodic table and was of the same order of magnitude as the gap between molybdenum and ruthenium (5.7), between which the element eka-manganese fell.[64] He pointed out that it was of approximately the same magnitude as the gap between osmium and tungsten (6.9), between which the element dvi-manganese fell.[65]

Brauner's point is clear. Given that these two elements below manganese were fully anticipated, even by Mendeleev, it is evident that the gap in atomic weight between neodymium and samarium points to another new element. One does not need Moseley's X-ray method or Moseley's law to make such a prediction. In the same paragraph, Brauner stated that he had predicted the discovery of seven elements, with atomic numbers 43, 61, 72, 75, 85, 87, and 89. This claim is quite remarkable given that even Moseley, armed with his experimental method and his law, was not able to reach this conclusion with anything like the degree of accuracy Brauner achieved, on purely chemical grounds, some 12 years prior. Moseley could only predict the existence of elements 43, 61, and 75 with any confidence.

The only difference between Brauner's sequence of seven elements and the seven elements that are the subject of the present chapter is his inclusion of element 89 and his omission of element 91. In fact, the isolation of element 89, which was eventually called actinium, had not been definitively settled when Brauner made his predictions in 1902.[66] The matter was not resolved until 1904 and only partly so. Brauner's only "mistake," therefore, was his failure to predict element 91.

Even in this case it is understandable why Brauner failed to predict the element. Unlike in other cases where he could search for large gaps between the atomic weights of consecutive elements, the atomic weight of element 91 presents a rare case of a pair reversal of which there are only five in the entire periodic table.[67] The atomic weights (modern values) of the three consecutive elements thorium (90), protactinium (91), and uranium (92) are 232.03, 231.035, and 238.02, respectively. On the other hand, perhaps Brauner could have predicted an element between thorium and uranium regardless of the pair reversal since the gap between thorium and uranium consists of almost exactly six units on the atomic weight scale.



Line	Cork, James,Fogg. 1926	Harris, Yntema, Hopkins. 1926	'real' element 61 1949
$L_{\alpha 1}$	2289		2287.9 ±0.4 XU
$L_{\alpha 2}$	2279	2278.1 ± 3.0	2277.5 ±0.3
$L_{\beta 1}$	2078	2077	2075.4 ±0.4
$L_{\beta 3}$	2038		2037.9 ±0.4
$L_{\beta 2}$	1952		1951.8 ±0.6
$L_{\gamma 1}$	1799		1795.2 ±0.9

FIGURE 11.13 Comparison of x-ray lines reported by Cork, James, and Fogg, with those for "real" element 61.

Finally, Brauner presents another argument, which he had mentioned in lectures to the Bohemian Chemical Society and to the St. Petersburg Academy, and which did not depend on gaps between atomic weights of elements in the periodic table. Brauner wrote that on arranging the true hydrides of the elements of the 8th series of the periodic system according to the order of their atomic weights, one finds the following remarkable regularity of the composition of these compounds:

CsH_1, BaH_2, LaH_3, CeH_4, PrH_3, NdH_2, XH_1, SmH_0

His conclusion was that since samarium does not combine with hydrogen, there must exist an unknown element between neodymium and samarium which forms the hydride XH_1 and that this element would be illinium.

An Italian Claim

In 1924, a team from Florence, Italy, believed that they had found element 61, although Luigi Rolla and Lorenzo Fernandes did not publish their findings until 1926. Writing in an Italian chemical journal that year, Rolla and Fernandes described the experiments on Brazilian monazite sand that they had begun in 1922. They wrote that their examination of the L series of the resulting X-ray spectra yielded no positive results. However, they also claimed that experiments on the K series of the same samples, carried out by a Professora Signorina Brunetti, yielded the characteristic frequencies for element 61. They explained that on first obtaining these results in June 1924, the quantity of the material they possessed was so small that they preferred to deposit the X-ray photographs in a sealed parcel at the Accademia dei Lincei rather than publish their results.[68]

They went on to describe how they had recently resumed their work on these samples and had carried out what seems today to be a staggering 3000 crystallizations in order to purify their suspected new element. The outcome of this work seems to have been a new series of spectra that showed the same spectral anomalies that had led them to suspect the presence of an element. The authors then conceded that they were going into print because of the recent announcement, from the United States, by J. Allen Harris, Smith Hopkins, and L. F. Yntema, who in the meantime had published their claim to having discovered the element they were calling illinium after their home state of Illinois.

In recent years, a group of Italians have written an interesting and detailed account of the work of Rolla and Fernandes.[69] Although they do not attempt to rehabilitate the work of their compatriots, they seem unable to resist giving at least some credit for the discovery of element 61 to both the Florentine and American teams.[70]

Charles James and B. Smith Hopkins

The next two authors who claimed to have discovered element 61 will be examined in parallel, even though they worked independently, because their stories are somewhat entwined. Whereas the majority of sources discuss the contribution of Smith Hopkins, few mention his contemporary, Charles James. This bias is partly due to the fact that Smith Hopkins published his claim in a more prominent journal, the *Journal of the American Chemical Society*, and perhaps also because he proposed a name for his element, something that the more retiring James did not do.[71]

I will start with Charles James, since he seems to have initiated his work on the rare earths, and element 61 in particular, before Smith Hopkins did. James was born in England and showed an interest in chemistry from a young age. While still in high school he wrote several letters to Sir William Ramsay, the University College chemist and discoverer of most of the noble gases. James began to search for element 61 following a letter from Ramsay in 1912, in which Ramsay pointed out that there were large gaps between the atomic weights of certain apparently consecutive elements in the periodic table. In particular, Ramsay singled out a suspected gap between the elements neodymium and samarium.[72]

At the even earlier date of 1908, James was corresponding with another British knight, Sir William Crookes, who was apparently analyzing some rare earth samples for James. James's connection with the British chemical intelligentsia is further highlighted by letters to and from Henry Moseley. In one of these letters, dated 1912, before Moseley's major breakthrough concerning atomic number, Moseley asked James to send him a sample of thulium. Clearly, James's search for element 61 did not need to wait for Moseley's definitive statement that a gap existed for this element.

James made his claim for the discovery of element 61 in the *Proceedings of the National Academy of Science* rather than in a mainstream chemistry journal. It was coauthored with his then graduate student at the University of New Hampshire, Herman Fogg, as well as James Cork of the Department of Physics at the University of Michigan, the last of whom carried out the X-ray spectral measurements on the samples provided by James and Fogg.

James's research program to search for element 61 had begun in 1923 and had used a variety of minerals, including gadolinite, ytterspar, and monazite. The work involved innumerable fractionations using many techniques that James himself had developed over many years and that were adopted by many other rare earth researchers. After uncovering what he termed "traces of element 61," James attempted to confirm the presence of the element using a large quantity of monazite, the ore that seemed to yield the most promising results. Finally, the fraction thought to contain the new element was sent to James Cork, an expert in making X-ray measurements on trace elements.

This final step involving cooperation with another university seems to have caused delays, as Cork took some time to get back to James with the results. In the meantime, James's competitor, Smith Hopkins, had already published his claim to the discovery of the element on the basis of what turned out to be less substantial X-ray evidence. Returning to James's and Cork's claim, the following X-ray spectral lines constitute the claim for what they believed to be element 61,

2.289, 2.279, 2.078, 2.038, 1.952, 1.799 and 1.725 X.U.

To put this into perspective, the authors also said that there were about twenty lines in the L series for each element, whereas only seven of them were fairly strong.

Remarkably, in 1949, two years after element 61, or promethium as it became known, was synthesized, a team from the Oak Ridge National Laboratory set out to determine the L spectrum of the "real element" and published their results in the *Physical Review*.[73] Moreover, they compared the spectrum of the element synthesized at Oak Ridge with the spectrum reported 23 years earlier by James, Fogg, and Cork. The results of this comparison, as well as a comparison with the lines obtained independently by Smith Hopkins, were presented in a table (see figure 11.13).

In spite of what seems to be a rather close coincidence between their own results and those of James, Fogg, and Cork, the Oak Ridge team gave no hint as to whether or not the measurements supported the earlier claims for the discovery of element 61.

Assuming the upper estimates of the 1949 measurements, by including the estimated errors as published by the authors in the table and rounding our values

$L_{\alpha 2}$	2288	2289
$L_{\alpha 1}$	2278	2279
$L_{\beta 1}$	2076	2078
$L_{\beta 3}$	2038	2038
$L_{\beta 2}$	1952	1952
$L_{\gamma 1}$	1796	1799

FIGURE 11.14
Based on W. F. Peed, K. J. Spitzer, and L. E. Burkhart, The L Spectrum of Element 61, *Physical Review*, 76, 143–144, 1949.

to coincide with the accuracy reported by Cork, James, and Fogg, we show how the two sets of values match up (see figure 11.14).

Two of these comparisons now represent an exact match, while a further two show a difference of just one unit in about 2300.[74] This may be why Clarence Murphy, writing as recently as 2006, also seems to support the claim that James might have actually discovered element 61.[75]

As mentioned above, Cork, James, and Fogg's paper was delayed because of the time that Cork took in sending his colleagues his measurements. But another perhaps even more significant factor conspired to weaken their claim. When James was almost ready to publish his own findings, he received a request from the editor of the *Journal of the American Chemical Society* to referee an article on the discovery of element 61 by Smith Hopkins at the University of Illinois. Rather than trying to find fault in this paper, James recommended publication to the editor but thereby prevented the possibility of his own submission, which would in all probability also have been made to this same journal.[76] In order to avoid any conflict of interest, James therefore submitted his own paper to the *Proceedings of the National Academy of Science*.[77] According to current estimates of the abundance of element 61 in the earth's crust, it appears that James could not have isolated the element, regardless of Murphy's attempt to rehabilitate James's claim.[78]

The Discovery of the "Real Element 61"

As mentioned earlier, the discoverers of element 61 did not deliberately set out to synthesize it. Rather, they were engaged in trying to identify various products of nuclear reactions that were being explored in the Manhattan Project.

The method they used was ion exchange chromatography, which involves separating the components in a mixture by using a solvent and some medium. For example, a column of a special material is used because it leads to different rates of movement of the components in the mixture.

Although ion exchange chromatography had begun as early as the 1850s, it was vastly improved during the Manhattan Project because of the need to separate numerous isotopes, including those of uranium and plutonium. The new feature was the use of special absorbents that could latch onto charged ions of the rare earth isotopes, which would then show different rates of elution within the selected column.

When Jacob Marinsky and Lawrence Glendenin, a postdoctoral and graduate student, respectively, began their work at MIT, they took up a finding that had been made in the Manhattan Project, which suggested that two unidentified fission products were present following the irradiation of a neodymium target. What was clear from these earlier studies was that the unidentified isotopes consisted of either praseodymium, neodymium, or element 61.

The ion exchange chromatography analysis by the pair from MIT made use of a synthetic organic cation exchanger called Amberlite IR, which consisted of a sulphonated phenol-formaldehyde compound. Experiments indicated that the order of elution was inversely related to the atomic number of the isotope in question. This can be seen in figure 11.15, in which elements 59, 58, and 57, or praseodymium, cerium, and lanthanum, respectively, are eluted. The higher atomic number isotope of 59, or praseodymium, is the first to be eluted, followed by cerium (58) and then lanthanum (57).

In a separate experiment containing only elements 59, 60, and 61 (the praseodymium group) in addition to yttrium, the various isotopes in question produced the elution peaks shown in figure 11.16. The peak at a volume of 1.6 liters was assigned to the element yttrium. Of the remaining four peaks, those corresponding to 2.8 liters were assigned to neodymium (element 60), while the tall peak at 3.6 liters was assigned to element 59, or praseodymium. Arguing by analogy with the previous diagram, and the inverse relationship between order of elution and atomic

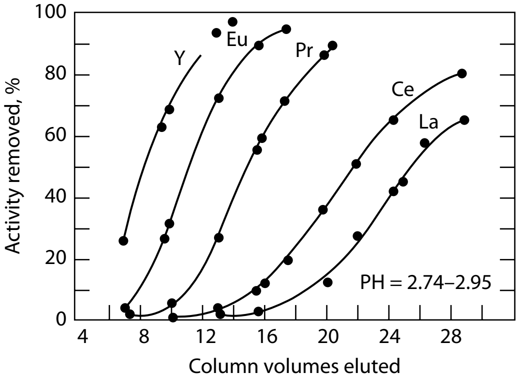


FIGURE 11.15 Ion-exchange chromatography and elution curves for various elements. Reprinted with permission of the American Chemical Society. From, J. A. Marinsky, L.E. Glendenin, C.D. Coryell, The Chemical Identification of Radioisotopes of Neodymium and of Element, *Journal of the American Chemical Society*, 69, 2781–2785, 1947.

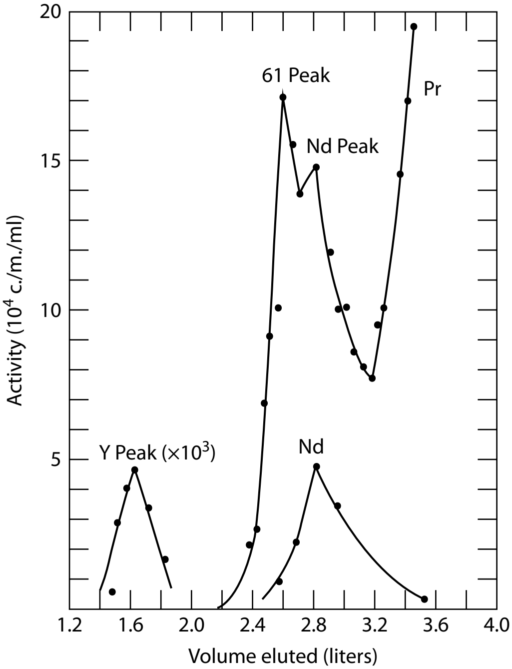


FIGURE 11.16
Elution curve of intermediate rare earth fraction. Reprinted with permission of the American Chemical Society. From, J. A. Marinsky, L.E. Glendenin, C.D. Coryell, The Chemical Identification of Radioisotopes of Neodymium and of Element, *Journal of the American Chemical Society*, 69, 2781–2785, 1947.

number, it was clear that the second tallest peak, corresponding to an activity of 17 units and a volume of about 2.6 liters, was due to an isotope of the new element with atomic number 61.

Two isotopes of element were discovered in these experiments. The first showed a half-life of 3.7 years corresponding to the peak just described and assigned to a mass number of 147, while further work revealed a shorter-lived isotope of mass number 149 with a half-life of 47 hours.

Element 61 in the periodic table represents a curious case in the same way that technetium does. It has an atomic number that is not especially high, and yet it took until 1945 for the element to be discovered. This is because the element is unusually unstable and in fact the only one of the 14 lanthanides ranging from La (57) to Yb (70) that is radioactive. The element is frequently described as being so unstable that it does not occur naturally on earth, but only on some stars. Or at least this is the standard account found in many books and Internet sources. The full story is inevitably far more complicated.

In fact, promethium does occur naturally on earth, in extremely miniscule amounts, in the mineral apatite as first reported in 1965 by Olavi Erämetsä,[79] followed by further reports by Paul Kuroda, who also found traces of the element in pitchblende in 1968. The amount reported by Kuroda and colleagues was (4 ± 1) x 10^{-15} grams of ^{147}Pm per kilogram of pitchblende.

Notes

1. Peter Atkins believes that cis-uranium would present a better alternative to my term. Although I agree that "cis" might be the opposite of "trans" to organic chemists, I prefer to stick to my original suggestion, which I believe to be more broadly accessible.

2. This is only true in principle. In fact, Moseley could only state that there were four missing elements with any confidence.

3. Another way to identify these elements would be to say that they were the seven missing elements between the limits of the "old periodic table" consisting of elements 1–92.

4. Mendeleev, as cited in J.R. Smith, *Persistence and Periodicity*, unpublished PhD thesis, University of London, 1975, p. 401.

5. This fact does not diminish Mendeleev's predictive abilities since he made ample use of horizontal trends in many other cases.

6. P. Thyssen, *Accommodating the Rare-Earths in the Periodic Table*, M.Sc. Thesis, Catholic University of Leuven, 2009.

7. As quoted by Sime in her book: R. Sime, *Lise Meitner, A Life in Physics*, University of California Press, Berkeley, CA, 1996.

8. With the exception of radium, Glenn Seaborg would eventually move all three of these elements as well as others to a different part of the periodic table. They came to form part of the actinide series, and it was realized that any apparent analogy with the third transition metal series was only partial.

9. Letter from Meitner to Hahn, October 25, 1916. This and subsequently cited letters are from the Otto Hahn Nachlass in the *Bibliothek und Archiv der Max-Planck-Gesselschaften*, Berlin-Dahlem.

10. O. Hahn, L. Meitner, Die Mutt ersubstanz des Actiniums, ein Neues Radioaktives Element von Langer Lebensdauer, *Physikalische Zeitschrift*, 19, 208–218, 1918.

11. It is very odd to see that many popular books and websites on the discovery of the elements insist on listing Soddy and Cranston as codiscoverers of element 91 and in some cases as the sole discoverers.

12. The history of this field is a complicated one that has essentially involved the multiplication of such elements from there being just four of them in the time of Mendeleev to the eventual discovery of a further 24, to make a total of 28 rare earth elements.

13. The priority dispute between Urbain and von Welsbach has been discussed by Helge Kragh among others: H. Kragh, in Elements No. 70, 71, and 72: Discoveries and Controversies, in C.H. Evans, (ed.), *Episodes in the History of Rare Earth Elements*, 67–89, Kluwer Academic Publishers, Norwell, MA, 1996.

14. The choice of the name "celtium" derives from the Celtic peoples, whose languages survive in parts of Wales, Ireland, and, most importantly for Urbain perhaps, in the French region of Brittany.

15. An associate of Maurice De Broglie, who was the brother of the founder of wave mechanics, Louis De Broglie.

16. As a matter of fact, they first proposed the name danium after Denmark. See H. Kragh, P. Robertson, On the Discovery of Element 72, *Journal of Chemical Education*, 56, 456–459, 1979.

17. Another reason for his choosing the name oceanium was as a mythological analogue of the element titanium, which lies two places above element 72 in the periodic table.

18. Anonymous, *The Times of London*, February 2, 1923.

19. Holland, where Coster came from, had also been neutral during the Great War and so could as such be regarded as being on the "wrong side." Hungary had been part of the Austro-Hungarian Empire and so was also regarded with suspicion.

20. Cited in G. Hevesy, *Adventures in Radioisotope Research*, Pergamon Press, Oxford, 1962, p. 11.

21. H.M. Hansen, S. Werner, Optical Spectrum of Hafnium, *Nature*, 111, 322–322, 1923

22. G. Urbain, Sur le celtium, élément de numero atomique 72, *Comptes Rendus de l'Académie des Sciences,* 176, 469–470, 1923.

23. W. Noddack, I. Tacke, O. Berg, Die Ekamangane, *Naturwissenschaften* 13(26), 567–574, 1925.

24. Today rhenium is extracted far more efficiently as the byproduct of the purification of molybdenum and copper.

25. Throughout this chapter we are using modern group numbers from 1–18.

26. P.H.M. van Assche, The Ignored Discovery of Element Z = 43, *Nuclear Physics*, A480, 205–214, 1988.

27. P.K. Kuroda, A Note on the Discovery of Technetium, *Nuclear Physics*, A503, 178–182, 1989.

28. H.K. Yoshihara, Discovery of a new element "nipponium": re-evaluation of pioneering works of Masataka Ogawa and his son Eijiro Ogawa, *Spectrochimica Acta Part B Atomic Spectroscopy*, 59, 1305–1310, 2004.

29. I am grateful to Javier Garcia Martinez, an inorganic chemist at the University of Alicante in Spain, for pointing out to me that Mendeleev initially predicted four rather than three elements. Garcia Martinez was the designer of an attractive postage stamp issued by Spain to commemorate the hundredth anniversary of Mendeleev's death in 2007. Also see D. Rabinovich, Mendeleev's Triumph, *Chemistry International*, 29 (July–August), 3, 2007; J. Garcia Martinez, P. Roman Polo, Spain Celebrates Its Year of Science, *Chemistry International*, 30, 4–8, 2008.

30. P. K. Kuroda, On the nuclear physical stability of the uranium minerals, *Journal of Chemical Physics*, 25, 781–782, 1956.

31. R. Bodu et al., Sur l'existence d'anomalies isotopiques rencontrés dans l'uranium du Gabon, *Comptes-rendus de l'Académie des sciences de Paris*, D 275, 1731–1736, 1972.

32. J. Newton Friend, *Man and the Chemistry of the Elements*, 2nd ed., Charles Griffin, London, 1961.

33. H. M. Van Assche, The Ignored Discovery of Element Z = 43, *Nuclear Physics A*, A480, 205–214, 1988.

34. Ibid.

35. Anonymous, The Disputed Discovery of Element 43. A Re-examination of an Elegant Early Use of Wavelength Dispersive X-ray Microanalysis, *Journal of Research of the National Institute of Standards and Technology*, 104 (November–December), 599–599, 1999.

36. It's Elemental, *Special 80th Anniversary Issue of Chemical & Engineering News*, September 8, 2003. Other articles that are relevant to the present book include one by the present author on hafnium (p. 138).

37. R. Zingales, From Masurium to Trinacrium: The Troubled Story of Element 43, *Journal of Chemical Education*, 82, 221–227, 2005.

38. F. Habashi, The History of Element 43—Technetium, *Journal of Chemical Education*, 83, 213–213, 2006. Habashi is also the author of a book dedicated to Ida Noddack. Fathi Habashi, *Ida Noddack (1896–1978)*, Laval University Press, Laval, Quebec, 2005. P. Kuroda, A Note on the Discovery of Technetium, *Nuclear Physics A*, 503, 178–182, 1989.

39. R. Zingales, The History of Element 43—Technetium (the author replies), *Journal of Chemical Education*, 83, 213–213, 2006.

40. F. Paneth, The Making of the Missing Chemical Elements, *Nature*, 159, 8–10, 1947. Although not nationalist in the usual sense, this comment is especially partisan given that

Paneth is reminding the reader that Noddack was a sympathizer with the Nazi regime. Nor is it difficult to appreciate why Paneth may have felt a good deal of resentment. He was dismissed from his own position as professor of inorganic chemistry by the Nazis in 1936, after which he fled to England, where he held positions at Imperial College and then Durham University. He did eventually return to Germany in 1953 to head the University of Mainz.

41. C. Perrier, E. Segrè, Technetium: The Element of Atomic Number 43, *Nature*, 159, 24–24, 1947; D. R. Corson, K. R. MacKenzie, E. Segrè, Astatine: The Element of Atomic Number 85, *Nature*, 159, 24–24, 1947.

42. E. Segrè, G.T. Seaborg, Nuclear isomerism in element 43, *Physical Review*, 54, 772–772, 1938.

43. S. Flugge, Kann der Energieinhalt der Atomkerne technisch nutzbar gemacht werden? *Naturwissenschaften*, 27, 402–410, 1939.

44. In fact, naturally occurring technetium had previously been discovered by Kenna and the same Paul Kuroda, in 1961, prior to the discovery of the Oklo reactor. B. T. Kenna, P. K. Kuroda, Isolating Naturally Occurring Technetium, *Inorganic and Nuclear Chemistry*, 23, 142–144, 1961.

45. I. Langmuir, Pathological Science, *Physics Today*, 42, 36–48, 1989.

46. G.B. Kauffman, J.P. Adloff, Marguerite Perey and the Discovery of Francium, *Education in Chemistry*, September 1989, 135–137.

47. L.A. Orozco, Francium, *Chemical & Engineering News*, 2003, http://pubs.acs.org/cen/80th/francium.html.

48. J.P. Adloff, G.B. Kauffman, Francium (Atomic Number 87), The Last Discovered Natural Element, *The Chemical Educator*, 10, 2005.

49. Recall that β emission produces an element with one unit of atomic number higher.

50. A couple of years earlier, Perrin had also presented an article by Hulubei entitled "Nouvelles recherches sur l'élement 87 (Ml)" to the same academy.

51. In 1953, E.K. Hyde in the United States discovered that there is a weak α decay in ^{223}Fr, which produces element 85. This means that, strictly speaking, even element 85, or astatine, occurs naturally, although its initial discovery was carried out via artificial synthesis.

52. B.F. Thornton, S.C. Burdette, Finding Eka-iodine: Discovery Priority in Modern Times, *Bulletin for the History of Chemistry*, 35, 86–96, 2010.

53. H.G. MacPherson, The Magneto Optic Method of Chemical Analysis, *Physical Review*, 47, 310–315, 1935.

54. H. Hulubei, Mesures du spectre L du Ra (88), *Comptes Rendus des Séances de l'Académie des Sciences*, Serie C, 203 , 542–543, 1936; H. Hulubei, Emissions faibles dans le spectre L du Ra (88), *Comptes Rendus des Séances de l'Académie des Sciences*, Serie C, 203, 665–667, 1936.

55. M. Valadares, Contributo Allo Studio Degli Spettri γ e X Molli dei Prodott di Disintegrazione del Radon, *Rendiconti Istituto Sanita Publicà*, 3, 953–963, 1942; M. Valadares, Gli spettri γ e X dei derivati del radon nella regione UX 700 a 1300, *Rendiconti Istituto Sanita Publicà*, 2, 1049–1056, 1941.

56. B. Karlik, T. Bernert, Zur Frage eines Dualen Zerfalls des RaA, Sitzber. *Akad. Wiss. Wien, Math.-naturw. Klasse*, 151, 255–265, 1942; B. Karlik, T. Bernert, Über eine Vermutete β-Strahlung des Radium A und die Natürliche Existenz des Elementes 85, *Naturwissenschaften*, 30, 685–686, 1942.

57. According to Thornton and Burdette's article of 2010, Paneth's motivations may have been somewhat nationalistic. They claim that Paneth supported the Austrians because he had been a former colleague of theirs at the Institute for Radium Studies. Whereas he had been forced to leave Germany, the Austrians Berta Karlik and Traude Bernert had

remained in the German territories, which of course included Austria, but Paneth was aware of Karlik's opposition to German war policies. In addition, they claim that Paneth was suspicious of the work of Hulubei and Cauchois, which was carried out in Nazi-occupied France, thus suggesting some form of compliance with German policies.

58. B. Karlik, Unsere Heutigen Kenntnisse über das Element 85 (Ekajod), *Monatshefte für Chemie*, 77, 348–351, 1947.

59. B.F. Thornton, S.C. Burdette, Finding Eka-iodine: Discovery Priority in Modern Times, *Bulletin for the History of Chemistry*, 35, 86–96, 2010.

60. Ibid.

61. Private correspondence from the authors.

62. D.R. Corson, K.R. MacKenzie, E. Segrè, Artificially Radioactive Element 85, *Physical Review*, 58, 672–678, 1940.

63. The country later became Czechoslovakia and, more recently, the Czech Republic.

64. Eventually, technetium was discovered in 1937.

65. In fact, Brauner claimed that dvi-manganese had recently been discovered by colleagues in his own institute. This is what he wrote in the letter to *Nature*: "As regards element No. 61, the difference between the atomic weights of Sm–Nd = 6.1, is greater than that between any other neighbouring elements. It is remarkable that it is of the same order as that between the atomic weights of Mo–Ru = 5.7, between which stands ekamanganese, and of Os–W = 6.9, between which stands dwi-manganese, recently discovered in our laboratory by Heyrovsky and Dolejsek."

66. André-Louis Debièrne, a French chemist, announced the discovery of a new element in 1899. He separated it from pitchblende residues left by Marie and Pierre Curie after they had extracted radium. Debièrne described the substance (in 1899) as similar to titanium and (in 1900) as similar to thorium. Friedrich Oskar Giesel independently discovered actinium in 1902 as a substance that was similar to lanthanum and called it "emanium" in 1904. After a comparison of substances in 1904, Debièrne's name was retained because it had seniority. The history of the discovery of actinium remained questionable for decades. Articles published in the 1970s and later suggest that Debièrne's results published in 1904 conflict with those reported in 1899 and 1900. Whether Debièrne and Giesel should share the honor of discovery or whether Giesel alone should be credited with the discovery is still under debate.

67. The five pair reversals consist of K and Ar, Co and Ni, Te and I, Th and Pa, and U and Np.

68. Author's translation: The material available to us was such a small quantity that we did not think it scrupulous to publish our findings and so we sent a small package containing our results, and the photos of the spectra that are under discussion, to the Academy of the Lincei.

69. M. Costa, M. Fotani, P. Manzelli, P. Papini, Storia della scoperta dell'elemento 61, in Storia e Fondamenti della Chimica, *Memorie di Scienze Fisiche e Naturali*, 1997, 441–442.

70. Author's translation: We hypothesize that the samples analyzed in Florence and America could have contained minimal traces of this element. One of the authors, Marco Fontani, has written to me and verified that this is a correct translation. He also writes that the phrase "minimal traces" was meant to refer to amounts that were undetectable either in the 1920s or as recently as the 1990s when this article was written. It should also be emphasized how the contemporary Italian authors show a refreshingly non-nationalistic attitude in crediting the American chemists to the same extent as their Italian compatriots.

71. My account is much indebted to a recent article by Clarence B. Murphy, who has had a long-standing interest in the discovery of element 61, as well as access to many archival sources belonging to both James and Smith Hopkins. C. J. Murphy, Charles James, B. Smith

Hopkins, and the Tangled Web of Element 61, *Bulletin for the History of Chemistry*, 31, 9–18, 2006.

72. This raises questions about Brauner's originality in recognizing this gap between atomic weights.

73. W.F. Peed, K.J. Spitzer, L.E. Burkhart, The L Spectrum of Element 61, *Physical Review*, 76, 143–144, 1949.

74. In his extended historical paper, which is very favorable to the claims of James et al., Clarence Murphy also fails to take a position on whether or not James had detected element 61, although he does say, "It is striking that the six lines reported by James and the two by Hopkins are remarkably close to those determined from an authentic sample of the element 61."

75. C.J. Murphy, Charles James, B. Smith Hopkins, and the Tangled Web of Element 61, *Bulletin for the History of Chemistry*, 31, 9–18, 2006.

76. The majority of James's articles on rare earth elements were published in the *Journal of the American Chemical Society*.

77. The paper by Smith Hopkins was received on April 26, 1925, and published on June 5, 1925. The one by Cork, James, and Fogg was published in December 1926.

78. As to the reliability of Cork, James's X-ray specialist working at the University of Michigan, I understand from a reliable source, who spent many years working in the same department, that the following joke was current among faculty members: If anybody was ever suspected of having messed up some piece of work, he or she was said to have "Corked it up!"

79. J.A. Marinsky, L.E. Glendenin, C.D. Coryell, The Chemical Identification of Radioisotopes of Neodymium and of Element 61, *Journal of the American Chemical Society*, 69, 2781–2785, 1947.

CHAPTER 12

SYNTHETIC ELEMENTS

The periodic table consists of about 90 elements that occur naturally ending with element 92 uranium. This lack of precision is deliberate since one or two elements such as technetium were first created artificially and only later found to occur naturally on earth. This kind of occurrence provides a foreshadowing of things to come when we begin to discuss the transuranium elements, meaning those beyond uranium that have been artificially synthesized.[1]

Chemists and physicists have succeeded in synthesizing some of the elements that were missing between hydrogen (1) and uranium (92). In addition, they have synthesized a further 25, or so, new elements beyond uranium, although, again, one or two of these elements, like neptunium and plutonium, were later found to exist naturally in exceedingly small amounts.

The existence of superheavy elements raises a number of interesting questions that pertain to the field of philosophy of science and also sociology of science. In fact, the very question of whether these superheavy elements actually exist needs to be dissected further, as it will be in the course of this chapter. The synthetic elements are extremely unstable, and only the lightest ones among them have been created in amounts large enough to be observed. Roughly speaking, the heavier the atom, the shorter its lifetime is. For example, the heaviest element for which there is now conclusive evidence is element 118, a few atoms of which have been created in just one single isotope form and with a half-life of less than a millisecond. Laypersons and specialists alike have asked themselves in what sense these elements can really be said to exist.

The superheavy elements also have philosophical implications for the study of the periodic system as a whole and the question of whether there is a natural end to chemical periodicity. A related question, which has now become quite pressing, is the possible extension of the periodic table to include a new g-block which in formal terms should begin at element 121.[2] Another interesting aspect is the question of the discovery of synthetic elements, or perhaps creation is a better word, since in general terms one can only discover something that already exists. As far as we know, none of the superheavy elements have ever been observed in any part of the universe.

Priority issues concerning superheavy elements have occurred in a large proportion of the 26 created elements. These priority issues are exacerbated by the fact that the elements are very unstable, but also because it is by no means clear what criteria should be used to determine precisely when a discovery or creation can be said to have occurred. Synthetic elements therefore have a role to play in the multifaceted question of what an element actually is.

As we will see in this chapter, the ways to specify experimentally the existence of an element have also changed over time. In addition to the well-known shift from atomic weight to atomic number that has been discussed in previous chapters, one now has to consider the duration for which an atom has to exist in order for it to be considered a genuine atom. It should be remembered that when superheavy nuclei are created, they do not initially have any attendant electrons. The time taken to acquire as many electrons as required to balance the nuclear charge amounts to 10^{-14} seconds. Consequently, the existence of new elements, capable of showing chemical behavior, at least in principle, is generally taken to refer to nuclei whose lifetime is at least 10^{-14} seconds.

In addition, given the enormous complexities involved in the production of these exotic atoms, the question of reproducibility needs to be revised accordingly. More specifically, the usual requirement for reproducibility that is applied in the discovery of other scientific phenomena need to be reconsidered. Some atoms have been officially ratified, even though they may not have been reproduced in other laboratories, because the observations have met the quality criteria that have been devised for the reliability of such experiments.

Perhaps one might even say that the field consists of more and more arguments about less and less substance, as the research has developed. As is well known, the technology required to artificially create new elements is extremely elaborate and expensive. Experiments typically take several years in order to form just a handful of atoms, which decay almost as soon as they have been created. Just as in the case of the seven elements discussed in chapter 11, bitter controversies and even a series of disputes have arisen that have been referred to as the transfermium wars.

The disputes concerning the priority in discovering superheavy elements have been amplified by a parallel set of disagreements concerning the names given to these new elements. In general, the discoverer of a phenomenon is traditionally granted the right to name the phenomenon in question. In the case of the superheavy elements, the need for independent adjudication of the true observation of any particular element has meant that the right to name an element is generally withheld from the "discoverers" until such a discovery can be approved. Even then, the governing bodies charged with making such decisions have sometimes objected to the names chosen by those who have been judged to have made the discoveries.

In several cases, both the discovery itself and the name of the element have been assigned by negotiation among experts in the relevant fields and eventually approved by committees such as IUPAC. This would seem to introduce an additional sociological aspect that is not generally found in typical scientific discoveries. Consensus among members of a committee, rather than just hard evidence, has sometimes been the deciding factor in the attribution of priority.

A further curious feature is that the synthesis of superheavy elements is largely a matter of nuclear physics. Although large teams of engineers and all kinds of other specialists are enlisted in the hunt for a particular element, most of the calculations and experiments are conducted by physicists. However, because one is dealing with elements, which are the domain of chemistry, the questions of priority and of the naming of elements have traditionally been assigned to chemists. Consequently, the superheavy element field raises new questions about the demarcation between chemistry and physics and whether there is any such difference in the final analysis.

The synthesis of many elements involves starting with a particular nucleus and subjecting it to bombardment with small particles, with the aim of increasing the atomic number and hence changing the identity of the nucleus in question. More recently, the method of synthesis has changed to involve the collision of nuclei of considerable weights but always with the aim of forming a larger and heavier nucleus. All such methods will be outlined below.

Early History of the Synthesis of Elements

Uranium represents the heaviest element among those that occur naturally. The element was first discovered in 1789. Mendeleev, as the leading discoverer of the periodic system, was responsible for correcting its atomic weight to a value of 240, a feature that established it as the heaviest element. Uranium is also distinguished because it was the element in which radioactive decay was first observed by Becquerel in 1896, as described in chapter 6.

Consequently, most chemists took it for granted that uranium would represent the limit of the periodic table and that any elements beyond uranium would be too unstable to exist naturally. Nevertheless, a succession of chemists and other scientists took a different view and openly discussed the notion of elements beyond uranium. In 1895, the Danish chemist Julius Thomsen speculated that uranium belonged to a 32-element period that terminated with an element of atomic weight of about 292.[3] In 1913, Johannes Rydberg, working in Sweden, discussed elements with high atomic numbers. For example, he predicted the atomic numbers of elements of the noble gases to include 168, 218, 290, 362, and 460.[4]

Whereas these speculations remained in the realm of possibilities, one of the first experimental claims to a transuranium element was published by Charles Baskerville at the University of North Carolina, whose examination of uranium salts led him to speculate about the existence of a new element with a weight of

255.8.[5] Baskerville went as far as to name the alleged element carolinium but, alas, his element was not to be.

A further series of theoretical studies were conducted by physicists beginning with Niels Bohr, who discussed the electronic configuration of elements terminating at atomic number 118.[6] However, Bohr also claimed that nuclei with a charge greater than 92 would not be sufficiently stable in order to exist under observable conditions. This prediction did not stop him from attempting to calculate the upper limit of the periodic system from the point of view of the electronic structure of atoms. In this way, he arrived at a value of 137, a figure that is banded about even these days as a rough estimate of the limits of the periodic table. A relativistic analysis carried out by Arnold Sommerfeld a little later also concluded that $Z = 137$ should signal the limit of the periodic table.[7]

In 1926, a relatively unknown German physicist, Richard Swinne, who is believed to have coined the term "transuranic elements," discussed the possible existence of elements up to number 118 and also believed that nuclear stability did not simply decrease with atomic number.[8] More specifically, he thought that long-lived elements would appear between the atomic numbers of 108 and 110. This idea can be regarded as an anticipation of the current views concerning islands of stability within the sequence of increasing atomic numbers.

In addition, several well-known physicists, including Walther Nernst[9] and James Jeans,[10] independently seeking to explain the energy of stars, speculated about the existence of elements with higher atomic weights than uranium. The earliest use of the term "superheavy element" can be found in a review article by Laurence Quill[11] in 1938 and in some articles by the physicist John Wheeler[12] from the 1950s, both of whom discussed the possibility of the existence of elements beyond uranium.

The Synthesis of Elements Beyond Uranium

The mother of all element formation experiments may be identified with a crucial experiment, conducted by Rutherford and Soddy, in 1919, at the University of Manchester. Rutherford and colleagues bombarded nuclei of nitrogen with α particles (helium ions), with the result that the nitrogen nucleus was transformed into that of another element and, although they did not realize it initially,[13] the reaction had produced an isotope of oxygen. In this way, Rutherford had achieved the first ever transmutation of one element into a completely different one. The dream of the ancient alchemists had become a reality, and this general process has continued to yield new elements up to the present time.

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H$$

However, this reaction did not produce a completely new element but just an unusual isotope of an existing element. While Rutherford used α particles produced by the radioactive decay of other unstable nuclei such as uranium, it soon emerged that similar transmutations could be carried out with target atoms other than nitrogen but extending as far as calcium with an atomic number of 20. If heavier nuclei were to be transmuted, it would require more energetic projectiles than naturally produced α particles.

The situation changed in the 1930s following the invention of the cyclotron by Ernest Lawrence at the University of California, Berkeley. This machine made it possible to accelerate α particles to hundreds and even thousands of times the speed possessed by naturally produced α particles. In addition, another projectile particle, the neutron, was discovered in 1932, having the added advantage of possessing a zero electric charge, which meant that it could penetrate a target atom without suffering any repulsion from the charged protons inside the nucleus.

In 1934 Enrico Fermi, working in Rome with Eduardo Amaldi, Emilio Segrè, and Oscar D'Agostino, began bombarding element targets with neutrons in the hope of synthesizing transuranium elements.[14] Here is how historian of science Ruth Sime begins an article on this research program:

> In 1934, when nuclear physics was young and the neutron had just been discovered, scientists embarked on a bold new project: the synthesis of artificial elements beyond uranium. The idea was straightforward—get a uranium nucleus to absorb a neutron and it will decay to the next higher element—but the work was difficult, even for the most expert nuclear physicists and radiochemists in the field. For a while they were successful, or so it seemed, as one transuranium element begat the next and the list kept growing. But in 1938, experiments suddenly revealed something much more interesting: uranium was not obediently producing new heavy elements, as everyone had thought, but instead was violently splitting into well-known lighter elements. The four-year search for transuranium elements in fact had been the study of fission fragments.

This event, which took place at the very start of the hunt for superheavy elements, highlights yet another reason for the importance of this subdiscipline. Although seeking heavier elements has virtually no practical consequences, the very discovery of nuclear fission, the basis for the subsequent development of nuclear weapons, as well as the peaceful use of nuclear power, all began from the innocent scientific question as to whether elements beyond uranium could be formed.

After hurling neutrons at the heaviest element uranium, Fermi and coworkers detected β emission, which they took to mean that they were progressing through higher atomic numbers within the periodic table.

Fermi believed that he had succeeded in producing two such elements, which he named ausonium (93) and hesperium (94), as shown in the first two steps of the following reaction,

$$_{92}U \rightarrow {}_{93}ekaRe \rightarrow {}_{94}ekaOs \rightarrow {}_{95}ekaIr$$

However, these researchers were mistaken, as were Hahn and Meitner, who initially believed that the observed β-decay indicated a gradual progression through ever higher atomic numbers such as 95 and 96.

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	RE	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

rare earths	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

FIGURE 12.1 The periodic table as it was assumed to be prior to Seaborg's suggestion of second series analogous to the lanthanides.

At this time, the periodic table was significantly different in that four elements, from actinium to uranium, were considered to be transition elements rather than part of a second series of f-block metals (figure 12.1). Fermi and his associates believed that their research showed the formation of eka-rhenium, eka-osmium, eka-iridium, eka-platinum, and eka-gold. The only significant critic of Fermi's claim was the German chemist Ida Noddack, who proposed that what was actually happening was the breakup of the nucleus to form elements that were already well known. This objection was an anticipation of nuclear fission that was not properly discovered until several years later. However, Noddack's idea was generally dismissed, first because she was a chemist and second because there existed no theory that supported the wholesale breakup of nuclei. The third, and perhaps most important, reason was that she along with her husband had developed something of a negative reputation after claiming to have discovered element 43 and for failing to withdraw their claim even after other researchers failed to replicate their alleged finding.

While physicists were wrong to think that the bombardment of nuclei with neutrons would only produce small changes rather than a major fragmentation or fission, chemists were still working with an incorrect periodic table in which the elements actinium, thorium, protactinium, and uranium were regarded as transition metals rather than the beginning of a series of elements analogous to the lanthanides.[15]

The explanation for the erroneous claims emerged one year later, in 1938, when Otto Hahn, Fritz Strassmann, and Lise Meitner discovered nuclear fission. It became clear that, on collision with a neutron, the uranium nucleus could break up to form two middle-sized nuclei rather than a larger one. For example, uranium-235 was capable of forming barium and krypton by the following fission reaction:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3\,^{1}_{0}n$$

Fermi and his collaborators had been observing such products of nuclear fission processes instead of forming heavier nuclei as they had first believed. Fortunately, Fermi was able to send the written version of his Nobel acceptance speech with a note to make the necessary correction, by stating that they had not in fact produced any transuranium elements.[16]

Real Transuranium Elements

The true identification of element 93 was finally carried out in 1939 by Edwin McMillan and his collaborators at Berkeley. This work was made possible by Ernest Lawrence's invention of the cyclotron. Instead of accelerating particles within straight-line motion, the cyclotron consisted of making particles move in circles of ever-increasing radii by the application of electric and magnetic fields, resulting in far higher velocities than had previously been achieved.

As research on nuclear fission progressed, McMillan decided to run an experiment bombarding uranium using the powerful 60-inch cyclotron. The purpose was to separate the various fission products produced by the bombardment, using the enormous force that the fragments gain from their mutual electrical repulsion after fissioning. McMillan observed two new beta decay half-lives in the uranium trioxide target, which suggested that whatever was producing the radioactivity had not repelled mutually like normal fission products. McMillan realized that one of the half-lives closely matched the known 23-minute decay period of uranium-239, but another observed half-life of 2.3 days was unknown. McMillan took the results of his experiment to his Berkeley chemistry colleague, Emilio Segrè, wanting to isolate the source of the radioactivity. The scientists worked under the assumption that element 93 would have similar chemistry to rhenium, but Segrè determined that McMillan's sample was not at all similar to rhenium. Instead, it behaved like members of the rare earth series of elements. Segrè and McMillan published an article with the title of "An Unsuccessful Search for Transuranium Elements." In 1940, McMillan and Philip Abelson again attempted to determine what was producing the unknown half-life, whereupon Abelson observed that whatever species was producing the 2.3-day half-life did not behave chemically like any known element and was more similar to uranium than a rare earth.[17]

This was the genuine new element 93 that was given the name of neptunium because it followed uranium in the periodic table just as the planet Neptune follows Uranus in terms of its distance from the sun. The discovery was openly announced in the *Physical Review* in 1940 since the wartime publication ban had not yet been imposed. On the basis of this discovery and similar findings on element 94, or plutonium, Glenn Seaborg proposed a major modification to the periodic table, as mentioned earlier. As a result, the elements from actinium (89) onward were no longer regarded as transition metals but as analogues of the lanthanide series. Consequently, there was no need for elements like 93 and 94 to behave like eka-rhenium and eka-osmium since they had migrated to different places on the revised periodic table.

Element 94, or plutonium, was created in late 1940 by Seaborg and his coworkers. This involved the initial production of Np-238, which subsequently decayed to form Pu-238:

$$^{238}_{93}Np \rightarrow ^{238}_{94}Pu + \beta^{0}_{-1}$$

They also produced another isotope of plutonium with a mass number of 239, which was found to be fissionable. This material would eventually provide a valuable alternative to the originally found fissionable isotope of U-238, which had to be separated from the nonfissionable U-235 by heroic means involving gas diffusion methods carried out on a vast industrial scale.[18] The existence of this particular transuranium element, plutonium, is in absolutely no doubt, given that approximately 400 tons of it are currently stockpiled in various places around the world.

The next two elements, 95 and 96, were synthesized in a similar manner using the Berkeley cyclotron. They were named americium (Am) and curium (Cm), respectively. For example, curium was obtained by the bombardment of Pu-239 with α particles:

$$^{239}_{94}Pu + ^{4}_{2}He \rightarrow ^{242}_{96}Cm + ^{1}_{0}n$$

The two elements had almost identical chemical properties, which made it difficult to separate them. Seaborg and coworkers informally joked about the elements being "pandemonium" and "delirium," respectively. The attempts to separate these two elements also led Seaborg to introduce an alternative form of the periodic table with a second series of f-block elements, starting at actinium, that was first published in *Chemical & Engineering News* magazine at the end of 1945.[19]

The decade ended with the synthesis of element 97, which was aptly named berkelium by its discoverers, followed by the synthesis of element 98, subsequently named californium, in 1950.

This sequence looked as though it was about to end since the heavier the nucleus, the more unstable it becomes. It became necessary to accumulate enough target material in the hope of bombarding it with neutrons in order to transform the element into a heavier one, at which point serendipity intervened. In 1952, a thermonuclear test explosion, codenamed Mike, was carried out close to the Marshall Islands in the Pacific Ocean. One of the outcomes was that intense streams of neutrons were produced, thus enabling such reactions as would not have been possible synthetically at this time. For example, the U-238 isotope can collide with 15 neutrons to form U-253, which subsequently undergo the loss of seven β particles, resulting in the formation of element 99, which was later named einsteinium:[20]

$$^{238}_{92}U + 15\,^{1}_{0}n \rightarrow ^{253}_{99}U \rightarrow ^{253}_{99}Es + 7\,^{-1}_{0}\beta$$

Element 100, named fermium, was produced in a similar manner as a result of the high neutron flux produced by the same explosion, and as revealed in the analysis of the soil from the nearby Pacific islands. In 1955, isotopes of both einsteinium and fermium were produced by a team in Berkeley led by Albert Ghiorso, who used a more conventional route consisting of a high-flux nuclear reactor that had then become available.

From 101 to 106

Advancing further along the sequence of ever heavier nuclei required a quite different approach, given that β decay does not take place for elements above $Z = 100$.

Several technological innovations were needed, including the use of linear accelerators rather than cyclotrons, the former allowing researchers to accelerate highly intense beams of ions at well-defined energies. The projectile particles could also now be heavier than neutrons or α particles. During the Cold War, the only countries that possessed such facilities were the two superpowers, the United States and the Soviet Union.

In 1955 mendelevium, element 101, was produced in this way at the linear accelerator at Berkeley:

$$^{253}_{99}Es + ^{4}_{2}He \rightarrow ^{256}_{101}Md + ^{1}_{0}n$$

However, only 17 atoms of Md-256 were formed in this manner, each of which was confirmed through their spontaneous fission following electron capture. This was also the first time that such an approach was used to confirm the presence of a particular element. Electron capture and spontaneous fission would go on to become the standard way of confirming the existence of many new elements. The American discoverers of element 101 decided to ignore the Cold War tension between the United States and the Soviet Union and named the new element mendelevium in honor of the Russian chemist Dmitri Mendeleev, the discoverer of the mature periodic system.

The Case of Nobelium

Unlike mendelevium which did not cause any priority dispute, the following element 102 was among the most bitterly fought, concerning which team could lay claim to its discovery. Whereas the first two decades of element synthesis had been dominated by US chemists and physicists, including McMillan, Seaborg, and Ghiorso, the first serious challenge from another nation arose in connection with element 102. A team of Swedish, American, and British physicists working at the Nobel Institute in Stockholm bombarded a uranium target in a 225 cm cyclotron. In 1957, these scientists announced the discovery of a new element that they proposed to call nobelium after Alfred Nobel. It was the first time that a claim had been made by European scientists and the first time that an international collaboration was involved in such a claim. Various newspaper and magazine articles followed suit and announced finding the element nobelium. However, this claim was not upheld but was followed by a priority dispute involving US and Soviet scientists. The nuclear chemist Paul Karol has called the discovery "the most convoluted and misunderstood of all the transfermiums."[21] The Berkeley team was unable to reproduce the results that had been obtained in Stockholm and began to wonder whether the Swedish element should be called "nobelenvium." A year later the US team claimed to have positively identified No-254 after bombarding a target made of curium with C-12 ions. At about the same time, researchers in the then USSR also denied the Swedish claim and over a period of several years also claimed to have their own definitive proof of the synthesis of element 102. This team was led by Georgii Flerov working at the Kurtachov Institute in Dubna, which would eventually be renamed the Joint Institute for Research (JINR). The American scientists refused to believe this claim but did not propose any alternative name for the element.

In 1961, the name nobelium was approved by the International Union of Pure and Applied Chemistry (IUPAC), even though no definite mass number had yet been associated with the claimed new isotopes. The Russians refused to accept this name and insisted on calling element 102 jolotium after Frédérique Joliot, the French nuclear physicist who happened to be an ardent communist.[22] The disputed discovery and name for this element finally reached resolution in the 1990s following several rounds of reviews by various committees.

Priority was initially granted to the Russian group by the transfermium working group (TWG), in a development that the Berkeley team flatly rejected. The more chemically inclined Seaborg and Karol, among others, strongly criticized this recommendation, while claiming that the physics-dominated TWG did not have sufficient understanding of the chemical aspects of superheavy elements. Not surprisingly perhaps, nationalistic factors also played a part in the dispute. For example, the nine members of the TWG that had decided in favor of the Russian claim consisted of one member from Japan and eight from Europe.

Finally, in 1997, IUPAC gave the credit for the discovery of element to the Russian team and retained the name of nobelium, which the Swedes had proposed 20 years earlier. As has been the custom in the past, the final word was granted to the chemists from IUPAC rather than to the physics-dominated transfermium working group.

Rather unsurprisingly, element 103 has also had a complicated history regarding where and when it was first discovered. It might be said to have been discovered over a period beginning as early as 1958 but only concluding in the mid-1990s. The element has been named lawrencium in honor of the United States' Ernest Lawrence, the inventor of the cyclotron. Until recently, the element was believed to be the final one among the actinide series, although this view is now disputed and some experts assign it and its lighter homologue, lutetium, to group 3 of the periodic table and so technically to the transition metals.[23]

Although credit for the discovery of the element was initially given to the US scientists led by Albert Ghiorso, serious doubts were later expressed about the earlier findings, especially by the rival team in Dubna. The Berkeley scientists arrived at their claim after bombarding a californium target with ions of boron:

$$^{252}_{98}Cf + ^{11}_{5}B \rightarrow ^{258}_{103}Lr + 5\,^{1}_{0}n$$

It was at this time that the Soviet team began to seriously challenge the monopoly that was held in California. The Flerov Laboratory of Nuclear Reactions was led by Georgii Flerov, a noted nuclear physicist who recruited a 28-year-old Armenian physicist, Yuri Oganessian, in 1961.[24] In 1965, the Soviet scientists carried out the synthesis of the element by means of the reaction,

$$^{243}_{95}Am + ^{18}_{8}O \rightarrow ^{256}_{103}Lr + 5\,^{1}_{0}n$$

The isotope of lawrencium so produced had a half-life of 45 seconds, although the Soviets initially preferred to call it rutherfordium. Credit for the discovery was granted to these Soviet scientists by the transfermium working group as late as 1992, with a rather telling statement that encapsulates how the attribution of priority becomes rather ambiguous in the field of superheavy elements,

> In the complicated situation presented by element 103, with several papers of varying degrees of completeness and conviction, none conclusive, and referring to several isotopes, it is impossible to say other than that full confidence was built up over a decade with credit attaching to the work in both Berkeley and Dubna.[25]

Element 104, or rutherfordium, was made in Berkeley in the course of the following reaction,

$$^{249}_{98}Cf + ^{12}_{6}C \rightarrow ^{257}_{104}Rf + 4\,^{1}_{0}n$$

while in Dubna, Russia, a different isotope of the same element was created in the reaction,

$$^{242}_{94}Pu + ^{22}_{10}Ne \rightarrow ^{259}_{104}Rf + 5\,^{1}_{0}n$$

As in the case of element 103, element 105, now known as dubnium, was claimed by both the Soviet and American teams, each of whom claimed to have produced a different isotope. As in the case of element 103, priority was eventually shared between both teams of scientists. Whereas the Soviets produced the element via the reaction between americium and neon, the American synthesis consisted of reacting californium with an isotope of nitrogen,[26]

$$^{243}_{95}Am + ^{22}_{10}Ne \rightarrow ^{256-x}_{105}Db + x\,^{1}_{0}n\left(x = 4\,or\,5\right)$$

$$^{249}_{98}Cf + ^{15}_{7}N \rightarrow ^{260}_{105}Db + 4\,^{1}_{0}n$$

Element 106, or seaborgium, is best known perhaps because of the storm of controversy that occurred when it came to naming it.[27] It was first claimed in 1974 by the Soviet team, now led by Oganessian, who collided together isotopes of lead and chromium,

$$^{208}_{82}Pb + ^{54}_{24}Cr \rightarrow ^{260}_{106}Sg + 2\,^{1}_{0}n$$

A few months later, the Berkeley team, including Seaborg and Ghiorso, obtained a longer lasting isotope of the same element using a different route,[28]

$$^{249}_{98}Cf + ^{18}_{8}O \rightarrow ^{263m}_{106}Sg + 4\,^{1}_{0}n$$

Credit was eventually assigned to the Berkeley team, which was also invited to propose a name. As Seaborg recalled later:

> [W]e were given credit for the discovery and the accompanying right to name the new element. The eight members of the Ghiorso group suggested a wide range of names honoring Isaac Newton, Thomas Edison, Leonardo da Vinci, Ferdinand Magellan, the mythical Ulysses, George Washington, and Finland, the native land of a member of the team. There was no focus and no front-runner for a long period.
>
> Then one day Al [Ghiorso] walked into my office and asked what I thought of naming element 106 "seaborgium." I was floored.[29]

What happened next can only be described as a farce. The American Chemical Society announced the name of element 106 as seaborgium at one of its national meetings in March 1994, but in August of the same year IUPAC announced that this name was unacceptable because no element could be named after a living person. Instead the IUPAC committee wanted to name the element rutherfordium. The result of this move was public outcry, both within the United States and further afield, and the mounting of a concerted campaign to recognize Seaborg's role.[30] In all, he had been the codiscoverer of something like 10 synthetic elements, starting with plutonium.

IUPAC began to yield to public pressure in 1995 and offered to name element 106 seaborgium, provided that the American team would abandon their proposed names for another set of elements that were under discussion at the time. It was only in August 1997 that IUPAC dropped these further conditions, while at the same time approving the naming of seaborgium.[31]

Partly as a result of Cold War tension between the United States and the Soviet Union, claims for the synthesis of most of these elements were hotly disputed, and these disputes continued for many years. In order to reach beyond element 106, a new approach was needed. It was at this point that German scientists entered the field, with the establishment of the Gesellschaft für Schwerionenforschung (GSI), or the Institute for Heavy-Ion Research, in Darmstadt. The new technology was named "cold fusion" but had nothing to do with the kind of cold fusion in a test tube announced by the chemists Martin Fleischmann and Stanley Pons in 1989.[32]

Cold fusion in the transuranium field is a technique whereby nuclei are made to collide with one another at slower speeds than were previously used. As a result, less energy is generated, and there is a decreased possibility that the combined nucleus can fall apart. This technique was originally devised by the Soviet physicist Yuri Oganessian but was developed more fully in Germany.

The "German Elements," 107–112

Element 107, eventually named bohrium, was the first of a sequence of elements for which the US and Russian monopoly on the synthesis of elements was finally broken by the GSI group in Darmstadt, Germany.

In 1976, the Russian group led by Yuri Oganessian had claimed the formation of element 107, but a lack of clear characterization of the isotopes produced meant that these experiments were not accorded any validity. In 1981, experiments in Darmstadt, led by Peter Armbruster and Gottfried Münzenberg, consisted of the bombardment of a bismuth target with accelerated ions of chromium, according to the following reaction:[33]

$$^{209}_{83}Bi + ^{54}_{24}Cr \rightarrow ^{262}_{107}Bh + ^{1}_{0}n$$

The German discoverers proposed the name of nielsbohrium, after the Danish physicist and pioneer of atomic structure. The discovery of the element was approved by the joint IUPAC/IUPAP (International Union of Pure and Applied Physics) committee together with the transfermium or TWG group in 1992. However, contrary to the discoverers' suggestion, the name of the element was changed to bohrium because no previous element had ever been given the full name of a scientist. The final announcement of the new element name was made in 1997.

Element 108 is now called hassium, after the German state of Hessen. Its most stable isotope is $^{270}_{108}Hs$, which has a half-life of about 10 seconds and of which more than 100 atoms have been produced. As in the case of element 107, the earliest claim for its discovery was made by the Russian group in Dubna after they had collided isotopes of radium and calcium in 1978 but with somewhat ambiguous results. The Darmstadt group published their findings in 1984, and were eventually approved as the official discoverers of the element via a different synthetic route,[34]

$$^{208}_{82}Pb + ^{58}_{26}Fe \rightarrow ^{265}_{108}Hs + ^{1}_{0}n$$

The element was given the provisional IUPAC name of unniloctium and a symbol of Uno in textbooks and on many periodic tables, although the scientists involved in synthesis work continued to call it element 108 or just 108. In 1992, the Darmstadt-based discoverers proposed the name hassium, after the German state in which the GSI institute is located.

In a surprising move in 1994, the IUPAC Nomenclature Committee recommended that the element be called hahnium, to honor Otto Hahn, one of the discoverers of nuclear fission, instead of what the GSI scientists had proposed.[35] However, following protests from the German discoverers, IUPAC changed its ruling, and the element was officially named hassium at the meeting of 1997 that also saw the approval of several other element names.

Element 109 now bears the official name of meitnerium and was actually synthesized two years before element 108, in a reaction that was replicated by the Russian group several years later.

$$^{209}_{83}Bi + ^{58}_{26}Fe \rightarrow ^{266}_{109}Mt + ^{1}_{0}n$$

The element was given the placeholder name of unnilennium and a symbol of Une. Unlike the case of so many other superheavy elements, the permanent name that was first proposed by the discoverer, meitnerium, was never disputed, although it, too, only gained official recognition at the IUPAC meeting held in 1997. It remains as the only element name that refers to a nonmythological woman. Although curium is generally thought to be in honor of Marie Curie, it was in fact named for the couple Marie and Pierre Curie.

Element 110 was also created at the GSI facility in 1994 as a result of the following collision reaction:[36]

$$^{208}_{82}Pb + ^{62}_{28}Ni \rightarrow ^{269}_{110}Ds + ^{1}_{0}n$$

Previous attempts in both Russia and the United States had led to some earlier claims. While the US scientists proposed the name hahnium, the Russians wanted to name this element becquerelium, after the discoverer of radioactivity. The German team that was responsible for the later, more substantiated claim proposed the name darmstadtium after the location of their institute, this being the name that eventually prevailed.

Element 111 is roentgenium, named after Wilhelm Röntgen, the discoverer of X-rays and the first recipient of the Nobel Prize for Physics in 1901. The first reliable synthesis of the element was achieved at the GSI center in Darmstadt, by means of the following reaction:[37]

$$^{209}_{83}Bi + ^{64}_{28}Ni \rightarrow ^{272}_{111}Rg + ^{1}_{0}n$$

that was carried out in 1994 and again in 2002.

Element 112, or copernicium, was named after the Polish astronomer Nicholaus Copernicus (1473–1543), who first proposed the heliocentric nature of the solar system. The element was first created by Sigurd Hofmann and coworkers at the GSI in Darmstadt by accelerating zinc ions onto a lead-208 target,[38]

$$^{208}_{82}Pb + ^{70}_{30}Zn \rightarrow ^{278}_{112}Cn^{\star} \rightarrow ^{277}_{112}Cn + ^{1}_{0}n$$

The discoverers initially proposed the symbol Cp, but this symbol had already been used for the element cassiopeium, which was eventually named lutetium ($Z = 71$). IUPAC asked the discoverers to propose an alternative symbol, and the symbol Cn was officially approved in 2010.

Elements 113-118

Since 1997, several claims have been published for the synthesis of elements 113 all the way to element 118, the most recent being element 117, synthesized in 2010. This is not surprising given that nuclei with an odd number of protons are invariably more unstable than those with an even number. The difference in stability

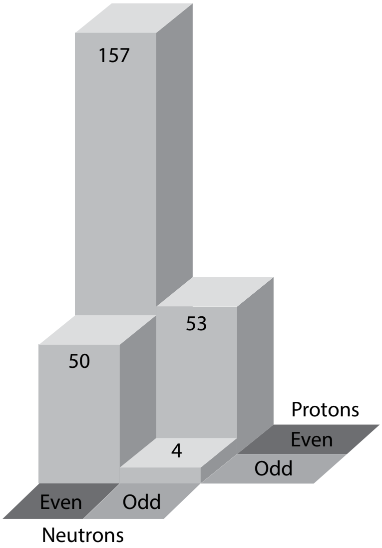


FIGURE 12.2
Nuclei with even numbers of both protons and neutrons account for the largest number of stable isotopes (157). Stable nuclei having an even number of just protons or just neutrons number 53 and 50 respectively. The smallest category consists of nuclei with an odd number of protons and also an odd number of neutrons. These stable nuclei number only 4. Reproduced from P.W.A. Atkins, L. Jones, L. Laverman, Chemical Principles, W.H. Freeman, New York, 2016, p. 753 (with permission).

occurs because protons, like electrons, have a spin of one-half and enter into energy orbitals, two-by-two, with opposite spins. It follows that even numbers of protons frequently produce total spins of zero and hence more stable nuclei than those with unpaired proton spins, as occurs in nuclei with odd numbers of protons such as 115 or 117 (figure 12.2).

Another general indicator of nuclear stability, which was mentioned in chapter 10, is the existence of magic numbers. Nuclei that have 2, 8, 20, 50, and 82 protons show enhanced stability due to possessing full nuclear energy levels, in a similar way that atoms possessing 2, 10, 18, 36, 54, 86, and 118 electrons, or the noble gas atoms, show greater stability because of their full electronic energy levels. Similarly, there are magic numbers for the number of neutrons present in a nucleus, namely, 2, 8, 20, 50, 82, or 126.

There are also nuclei that are said to be doubly magic in that they have magic numbers with respect to both protons and neutrons. Examples include ^{16}O, ^{48}Ca, and ^{208}Pb. However, such combinations do not always produce enhanced stability. For example, one might have expected $^{132}_{50}Sn$ to be stable due to its being doubly magic, and yet it has a half-life of only 39.7 seconds. In fact, double magicity is neither necessary nor sufficient for stability. Just as it is possible for a nucleus to be doubly magic and not to be stable, so there are isotopes that are stable but do not have a doubly magic number of protons and neutrons.

More specifically, in the mid-1960s it was predicted that there might be some deviations from the classic magic numbers cited above in the case of superheavy elements. In particular, nuclear physicists have generally agreed that a nucleus with 114 protons should also behave magically.[39] The synthesis of this element was therefore much anticipated because it would represent the center of an "island of stability," that is, a portion of the table of nuclei with enhanced stability. In fact, this prediction contributed significantly to a revival of interest in the synthesis of superheavy elements, since 114 was clearly more attainable than the classically predicted magic number of 126.

Element 114 was first claimed by the Dubna lab in late 1998 but only definitely produced in further experiments in 1999 involving the collision of a plutonium target with ions of calcium-48.[40] The labs at Berkeley and Darmstadt have recently confirmed this finding. At the time of writing, nearly 80 decays involving element 114 have been reported, 30 of which come from the decay of heavier nuclei such as 116 and 118. The longest-lived isotope of element 114 has a mass of 289 and a half-life of about 2.6 seconds, in agreement with predictions that this element would show enhanced stability. Nevertheless, the enhanced stability of this element is nowhere near the expectations initially discussed in the 1960s.

On December 30, 1998, the Dubna-Livermore labs published a joint paper, claiming element 118 had been observed as a result of the following reaction:

$$^{208}_{82}Pb + ^{86}_{36}Kr \rightarrow ^{293}_{118}Uno + ^{1}_{0}n$$

After several failed attempts to reproduce this result in Japan, France, and Germany, the claim was officially retracted in July 2001. Much controversy followed, including the dismissal of one senior member of the research team who had published the original claim.[41]

A couple of years later, new claims were announced from Dubna and were followed in 2006 by further claims by the Lawrence Livermore Laboratory in California. Collectively, the US and Russian scientists made a stronger claim that they had detected four more decays of element 118 from the following reaction:

$$^{249}_{98}Cf + ^{48}_{20}Ca \rightarrow ^{294}_{118}Uno + 3\,^{1}_{0}n$$

The researchers are highly confident that the results are reliable, since the chance that the detections were random events was estimated to be less than one part in 100,000. Needless to say, no chemical experiments have yet been conducted on this element, in view of the paucity of atoms produced and their very short lifetimes of less than one millisecond.

In 2010, an even more unstable element, number 117, was synthesized and characterized by a large team of researchers working in Dubna, as well as several labs in the United States.[42] The periodic table has reached an interesting point at which all 118 elements exist either in nature or have been created artificially in special experiments, including a remarkable 26 elements beyond the element uranium. At the time of writing, there are even plans to attempt the creation of yet heavier elements such as 119 and 120, and there are no reasons to think there should be any immediate end to the sequence of elements that can be formed.

Chemistry of the Synthetic Elements and Relativistic Effects

The existence of superheavy elements raises an interesting new question and also a challenge to the periodic table. It also affords an intriguing new meeting point for theoretical predictions to be pitted against experimental findings. Theoretical research suggests that the effects of relativity become increasingly important as the nuclear charge of atoms increases. For example, the characteristic color of gold, with a rather modest atomic number of 79, is now explained by appeal to the theory of relativity. The larger the nuclear charge, the faster the motion of inner-shell electrons. As a consequence of gaining relativistic speeds, such inner electrons are drawn closer to the nucleus, and this in turn has the effect of causing greater screening on the outermost electrons which determine the chemical properties of any particular element. It has been predicted that some atoms should behave chemically in a manner that is unexpected from their presumed positions in the periodic table.

Relativistic effects thus pose the latest challenge to test the universality of the periodic table. Such theoretical predictions have been published by various researchers over a period of many years, but it was only when elements 104 and 105, rutherfordium and dubnium, respectively, were chemically examined that the situation reached something of a climax. It was found that the chemical behavior of rutherfordium and dubnium was in fact rather different from what one would expect intuitively based on where these elements lie in the periodic table. Rutherfordium and dubnium did not seem to behave like hafnium and tantalum, respectively, as they should have done.

For example, in 1990, Kenneth Czerwinski, working at Berkeley, reported that the solution chemistry of element 104, or rutherfordium, differed from that of zirconium and hafnium, the two elements lying above it. Meanwhile, he also reported that rutherfordium's chemistry resembled that of the element plutonium that lies some distance away in the periodic table. As to dubnium, early studies showed that it, too, was not behaving like the element above it, namely, tantalum, but showed greater similarities with the actinide element protactinium. In other experiments, however, rutherfordium and dubnium seemed to be behaving more like the two elements above hafnium and tantalum, namely, zirconium and niobium.

TABLE 12.1
Fragment periodic table showing groups 3–12 inclusive.

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
Lu	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
Lr	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**

When the chemistry of seaborgium (106) and bohrium (107) was examined, it showed that the expected periodic behavior was resumed. The titles of the articles that announced these discoveries spoke for themselves. They included "Oddly Ordinary Seaborgium"[43] and "Boring Bohrium,"[44] both referring to the fact that it was business as usual for the periodic table. Even though relativistic effects should be even more pronounced for these two elements, the expected chemical behavior seems to outweigh any such tendencies.

The fact that bohrium behaves as a good member of group 7 can be seen from the following argument that I have proposed. This approach also represents a kind of "full circle" since it involves a triad of elements. As the reader may recall from chapter 3, the discovery of triads was the very first hint of a numerical regularity relating the properties of elements within a common group. The data for measurements carried out on the standard sublimation enthalpies of the analogous compounds of technetium, rhenium, and bohrium with oxygen and chlorine (energy required to convert a solid directly into a gas) are shown in table 12.2.[45]

Predicting the value for BhO_3Cl using the triad method gives 83 kJ/mol, or an error of only 6.7% compared with the above experimental value of 89 kJ/mol. This fact lends further support to the notion that bohrium acts as a genuine group 7 element (table 12.3).

The challenge to the periodic law from relativistic effects became even more poignant in the case of number 112, or copernicium, the most recent element for which chemical experiments have been conducted.[46] Once again, relativistic calculations indicated modified chemical behavior to the extent that the element was thought to behave like a noble gas rather than like mercury below which it is placed in the periodic table. Experiments carried out on sublimation enthalpies on element 112 then showed that, contrary to earlier expectations, the element truly belongs in group 12 along with zinc, cadmium, and mercury, as shown in figure 12.3.

TABLE 12.2
Standard sublimation enthalpies of compounds of technetium, rhenium and bohrium.

TcO_3Cl = 49 kJ/mol
ReO_3Cl = 66 kJ/mol
BhO_3Cl = 89 kJ/mol

TABLE 12.3
Second, third, and fourth members of Group 7.

Tc
Re
Bh

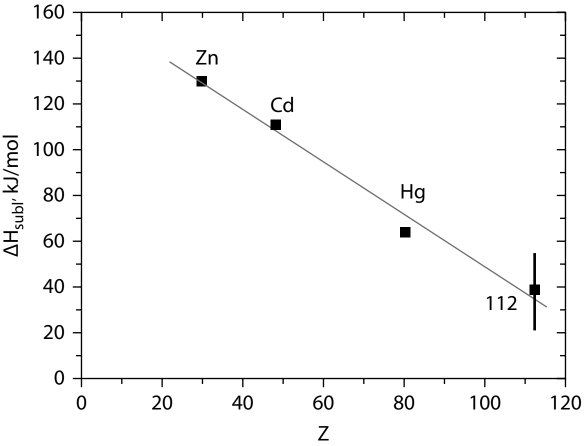


FIGURE 12.3 Sublimation enthalpies for elements in group 12 showing that element 112 is a genuine member of this group.

Element 114 presented a similar story, with early calculations and experiments suggesting noble gas behavior but more recent experiments supporting the notion that the element behaves like the metal lead as expected from its position in group 14. The conclusion would seem to be that chemical periodicity is a remarkably robust phenomenon. Not even the powerful relativistic effects due to fast-moving electrons seem to be capable of toppling a simple scientific discovery that was made around 150 years ago.

Moreover, at least for the foreseeable future, it does not look as if relativity theory is about to cause a major upset to the periodic table. This is because relativistic effects do not simply increase with increasing atomic number. It is more a case of the interplay of relativistic effects and quantum effects that govern the particular order of energy levels in any given atom. For example, in the sixth period, the largest relativistic effect occurs at the atoms of gold and not at the end of the period where the atomic number is even higher (figure 12.4). This effect has been termed the "gold maximum" phenomenon by Pekka Pyykkö, the Finnish chemist and leading expert in relativistic quantum chemistry. It is the ability of the element gold to show the largest relativistic effect of any element in its period that causes it to display anomalous chemical and physical properties. For example, gold displays a characteristic golden-yellow color, unlike any of its surrounding transition metals in the periodic table. It also shows an anomalous voltage when it is used to make up an electrical cell, and it has a tendency to form unusual oxidation states and a host of unexpected new compounds, many of which were predicted by Pyykkö.[47]

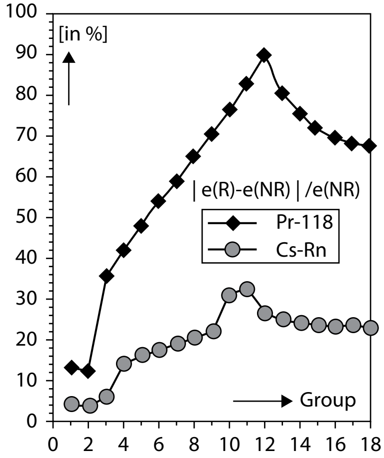


FIGURE 12.4
The gold maximum effect (circles) and the analogous effect in the next period at element 112 (diamonds). Reproduced from P. Schwerdtfeger et al. The Encyclopedia of Computational Chemistry, eds. P v. R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, H.F. Schaefer III, P.R. Schreiner, John Wiley and Sons, New York, 1998 (with permission).

Calculations carried out by others have shown that in period seven the maximum relativistic effect should take place at element 112.[48] As can be seen from figure 12.4, the effect then drops away rather sharply for subsequent elements. The fact that the chemistry of elements 112 and 114 has been examined and that results show no signs of highly anomalous behavior would seem to suggest that the chemistry of the subsequent elements should also behave as expected on the basis of the periodic table. The very fact that the gold maximum, or greatest relativistic effect in the period recurs at element 112, is surely a consequence of periodicity itself, and so it is further testament to the underlying fundamental nature of the periodic law. This law continues to stand firm against the threats from quantum mechanics and relativity combined together.

Finally, Something Completely Different

In 2017, a paper was published involving a collaboration between scientists in various countries, aimed at exploring element 118 or oganesson, which is currently the heaviest atom ever produced.[49] The predictions indicate rather extreme relativistic effects, which show that this atom may not have electrons in shells as is the norm for all previous atoms. The electrons are expected to form a kind of soup. As a result the periodic table will become even more irrelevant when it comes to predicting the properties of the atom than the kinds of relativistic effects that have been known to occur in elements such as gold and lead or dubnium and rutherfordium.

But even more startlingly, the calculations carried out by this team led by New Zealander Peter Schwerdtfeger indicate that at certain even higher atomic numbers there will come a point at which nuclei will not even have any electrons, regardless of whether they occur in shells or otherwise. If this is correct, it would mean the end of chemistry in an even more profound sense since chemical behavior is governed by the electrons in an atom. Finally and even more bizarrely, these predictions indicate that at certain atomic number values atoms accompanied with electrons will begin to appear once again. This implies that the periodic table would have genuine gaps in which there are no atoms, as we generally know them, that are capable of showing chemical behavior.

Concluding Speculations

I conclude this chapter with a little philosophical speculation that is partly inspired by issues concerning the synthetic elements and will also address some earlier themes concerning the nature of elements. As we have seen in this chapter, part of the controversy concerning synthetic elements has to do with conflicting views among chemists and physicists about what constitutes a genuine atom and hence a genuine element. I believe that this issue points to something deeper that also concerns chemical education and the philosophy of chemistry.

It is a rather paradoxical fact that the identity of any element is determined by the nucleus of its atoms or, more precisely, by the number of protons. On the other hand, chemical behavior is determined exclusively by the electrons orbiting the nucleus. When considered from a more philosophical perspective, however, some of this apparent paradox is alleviated. It is essential that any feature that governs identity should be associated with something that does not change under the course of normal chemical reactions. Whereas the number of protons does not change, unless one considers nuclear transformations, the number and arrangement of electrons can undergo all manner of changes.

There is another apparent paradox concerning elements. Stoichiometric calculations are carried out using the atomic weights of elements, whose values are made up almost exclusively by the mass of the nuclei concerned. Electrons do contribute, but by a factor of about 2000 times less than protons and neutrons, given their correspondingly lower masses. On the other hand, the manner in which elements and compounds react is again due to the electrons in an atom or a compound. Whereas the amount produced in a chemical reaction seems to depend largely on the nucleus, what is produced depends upon the electrons.

Of course, this is an oversimplification of the facts. In reality, the chemistry of an element depends on the dynamical behavior of the electrons surrounding a particular nucleus with a specific atomic charge. Stated in more quantum mechanical terms, any attempt to calculate the properties of atoms, such as their total energy, is based on the Hamiltonian operator, which involves Coulombic interaction terms to reflect internuclear and interelectronic repulsions, as well as attractions between electrons and protons.

As the reader may recall from chapter 4, philosophers of chemistry have conducted an ongoing debate concerning the dual nature of elements. In the terminology of Paneth, one can identify an element as a basic substance that is the unchanging "bearer of properties" and that can be given a microscopic interpretation as the atomic charge or Z. The other philosophical sense of the term "element" is that of an element as a simple substance, meaning the uncombined element that can actually be isolated, such as metallic sodium or diatomic chlorine gas. This sense of element can be identified with the nuclear charge plus an equal number of accompanying electrons.

It is often claimed that Mendeleev attributed greater importance to elements as basic substances than as simple substances when he arrived at his views on chemical periodicity and the periodic table. As Mendeleev states explicitly in many passages, when we invoke the element carbon, for example, what is intended is the abstract form of carbon that underlies both graphite and diamond.

However, the view that the periodic table is based primarily based on this sense of the term "element" may be an oversimplification on the part of Mendeleev since it is not fully consistent with the very notion of chemical periodicity. In order to identify chemical periodicity, one has no choice but to also focus on the manner in which elements react, rather than on the essence of elements (basic substance). It would appear that chemical periodicity, and hence the periodic table, are a reflection of both the simple and basic substance aspects of elements. To concentrate exclusively on elements as basic substances would result in placing the elements in a one-dimensional list rather than a two-dimensional arrangement that reflects chemical repetitions.

Consequently, it is not a matter of the number of protons or the number of electrons, or even the number of protons as opposed to the sum of the protons and electrons in any atom. Rather, it is a matter of the interaction between the protons and the accompanying electrons as reflected in the quantum mechanical approach alluded to above.

No doubt there are several loose ends in these brief speculations that are intended to show that the book is far from being closed on questions concerning elements, the periodic table, and the role of quantum mechanics in providing an explanation for chemical behavior.

Notes

1. Although there is as yet no authoritative history of superheavy elements, Helge Kragh has recently published a monograph from which I have drawn in writing this chapter. H. Kragh, *From Transuranic to Superheavy Elements, A Story of Dispute and Creation*, Springer, Cham, Switzerland, 2018.

2. P. Karol, Heavy, Superheavy…Quo Vadis, in E.R. Scerri, G. Restrepo, *From Mendeleev to Oganesson*, Oxford University Press, Oxford, 2018, pp. 8–42.

3. H. Kragh, *From Transuranic to Superheavy Elements, A Story of Dispute and Creation*, Springer, Cham, Switzerland, 2018, p. 6.

4. Rydberg was one of the first scientists to take up van den Broek and Moseley's discovery that the more accurate criterion for ordering the elements was atomic number rather than atomic weight.

5. C. Baskerville, On the Existence of an Element Associated with Thorium, *Journal of the American Chemical Society*, 23, 761–774, 1901.

6. N. Bohr, The Structure of the Atom, *Nature*, 112, 29–44, 1923.

7. This result comes as something of a surprise since it implies that the inclusion of special relativity has no effect on the stability of atoms.

8. R. Swinne, Zum Ursprung der durchdringenden Höhenstrahlung, *Naturwissenschaften,* 7, 529–530, 1919.

9. W. Nernst, Physico-Chemical Considerations in Astrophysics, *Journal of the Franklin Institute*, 206, 135–142, 1928.

10. J. Jeans, *Astronomy and Cosmogony*, Cambridge University Press, Cambridge, 1928.

11. L.L. Quill, The Transuranium Elements, *Chemical Reviews* 23, 87–155, 1938.

12. J.A. Wheeler, Nuclear Fission and Nuclear Stability, in *Niels Bohr and the Development of Physics*, Wolfgang Pauli (ed.), Pergamon Press, London, 1955, pp. 163–184.

13. Rutherford initially believed that his team had formed an isotope of carbon. E. Rutherford, Collisions of Alpha Particles with Light Atoms. IV. An Anomalous Effect in Nitrogen, *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science*, 6th series, 37, 581ff., 1919.

14. E. Fermi, Possible Production of Elements of Atomic Number Higher Than 92, *Nature*, 133, 898–899, 1934.

15. Jeremy Bernstein, *Plutonium, A History of the World's Most Dangerous Element*, Joseph Henry Press, Washington, DC, 2007.

16. It appears that Fermi was more cautious than his colleagues about whether they had in fact produced any transuranium elements. Gino Segre, Bettina Hoerlin, *The Pope of Physics*, *Enrico Fermi and the Birth of the Atomic Age*, Picador, 2016.

17. E. McMillan, P. Abelson, Radioactive Element 93, *Physical Review* 57, 12, 1185, 1950.

18. The second atomic bomb dropped on Japan fell on the city of Nagasaki and was a plutonium bomb.

19. It should be said, however, that the possibility of a second series analogous to the rare earth elements had already been anticipated by a number of authors, including Alfred Werner, Charles Janet, and Laurence Quill, but for different reasons. A. Werner, Beitrag zum Ausbau des periodischen Systems, *Berichte*, 38, 914–921, 1905; C. Janet, *Concordance de l'arrangement quantique de base des électrons planétaires des atomes avec la classification scalariforme hélicoıdale des elements chimiques*, Beauvais Imprimerie Départementale de l'Oise, Beauvais, 1930; L.L. Quill, The transuranium elements, *Chemical Reviews* 23, 87–155, 1938. Also see a chapter on Janet in E.R. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, 2016, pp. 149–170.

20. P.R. Fields; M.H. Studier; H. Diamond; J.F. Mech; M.G. Inghram; G.L. Pyle; C.M. Stevens; S. Fried; W.M. Manning; A. Ghiorso; S.G. Thompson; G.H. Higgins; G.T. Seaborg, Transplutonium Ir Elements in Thermonuclear Test Debris, *Physical Review* 102(1), 180–182, 1956.

21. P.J. Karol, in D.H. Rouvray, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Research Studies Press, Baldock, UK, 2004, 235–262.

22. The name Joliotium was later also proposed for elements 103 and 105, but to this day no element bears this name.

23. The placement of lutetium and lawrencium is discussed more fully in the following chapter on alternative periodic tables.

24. Both physicists now have elements named after them, although in the case of flerovium, the naming was meant to honor the Flerov Institute, a precursor of the Joint Institute for Nuclear Research (JINR) rather than Flerov the person.

25. R.C. Barber, N.N. Greenwood, A.Z. Hrynkiewicz, Y.P. Jeannin, M. Lefort, M. Sakai, I. Ulehla, A.H. Wapstra, D.H. Wilkinson, Discovery of the Transfermium Elements, *Progress in Particle and Nuclear Physics*, 29, 453–530, 1992.

26. The symbol for element 105 is shown here as Db for the sake of clarity only. The originally reported research would have used 105 since no name or symbol had yet been approved.

27. On the general question of the naming of elements, see W.H. Koppenol, Paneth, IUPAC, and the Naming of Elements, *Helvetica Chimica Acta*, 88, 95–99, 2005.

28. The m in the mass number denotes the presence of a metastable isotope of the element. The half-life in this particular case was 0.9 second, as compared with the earlier Soviet claim of 4–10 milliseconds.

29. G. Seaborg, quoted in G.T. Seaborg, E. Seaborg, *Adventures in the Atomic Age: From Watts to Washington*, Farrar, Straus and Giroux, New York, 2001.

30. I can personally recall signing a petition at an American Chemical Society (ACS) meeting where many participants were wearing lapel badges bearing the symbol of Sg in support of naming the element after the beloved Berkeley professor who, among other things, had been a scientific advisor to 10 US presidents. I also recall asking Seaborg a question after he had spoken at an ACS meeting in Las Vegas in 1997 and being taken by the way he responded by inviting me for lunch, during which time he displayed a degree of simplicity and modesty that seems to mark exceptionally accomplished scientists.

31. Seaborg lived for a further 18 months before passing away in 1999 at the age of 86.

32. M. Fleischmann, S. Pons, Electrochemically Induced Nuclear Fusion of Deuterium, *Journal of Electroanalytical Chemistry*, 261(2A), 301–308, 1989.

33. G. Münzenerg; S. Hofmann; F.P. Hessberger; W. Reisdorf; K.H. Schmidt; J.H.R. Schneider; P. Armbruster; C.C. Sahm, et al., Identification of element 107 by α correlation chains, *Zeitschrift für Physik A* 300, 107, 1981.

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35. They also recommended that element 109 be called meitnerium, so that the two discoverers of fission would have occupied positions next to each other in the sequence of elements. But it was not to be. Hahn no longer has an element named after him, a fact that perhaps goes some way to rectifying the injustice of his obtaining a share of the Nobel Prize for the discovery of fission, whereas Meitner did not. Nor, it should be added, did Hahn speak up on her behalf.

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CHAPTER

13

FORMS OF THE PERIODIC TABLE

A good deal has been said about the periodic table in previous chapters, but one important aspect has not yet been addressed. This is the question of why so many different periodic tables have been published in textbooks, articles, and on the Internet. One may also wonder whether there exists an "optimal periodic table" and whether such a question even makes sense. Assuming it is a legitimate question, one would like to know what progress has been made toward identifying such an optimal table.

Before plunging into this further aspect of chemical periodicity, at least two kinds of differences among periodic tables should be distinguished. First, there is the question of whether the table is presented as having 8, 18, 32, or even higher numbers of columns. Second, there is the question of variations among tables concerning the placement of specific elements such as hydrogen, helium, lanthanum, actinium, lutetium, and lawrencium.

In a classic, though flawed, book on the history of the periodic table, Edward Mazurs included illustrations as well as references to about 700 periodic tables that have been published since the periodic table was first assembled in the 1860s.[1] In the 45 or so years that have elapsed since the publication of Mazurs's book, at least another 300 tables have appeared, not to mention the numerous new periodic systems posted on the Internet.[2] The fact that so many periodic tables exist is something that requires an explanation. Of course, many of these tables may not have anything new to offer, and some are even inconsistent from a scientific point of view. But even if we were to eliminate these misleading proposals, a very large number of tables still remain.

Differences in Numbers of Columns

In chapter 1, we saw that there are three basic forms of the periodic table: the short form, the medium-long form, and the long form. All three convey very much the same information, although the grouping of elements with the same valence is treated differently in each of these formats. Mendeleev and the others who discovered chemical periodicity in the 1860s generally presented their findings in the form of an 8-column table or what has become known as a short-form table (figure 4.4).[3] This format has several appealing features which are worth pausing to consider. The first virtue is the simplicity of the short form. It is based on the notion that chemical and physical properties recur approximately after eight elements and continue to do so. Unfortunately, some of the simplicity and directness of this presentation is lost when one moves to the 18-column format (figure 1.5) or even wider periodic tables.

A second virtue is that the 8-column table groups together a wide range of elements that share the same highest valency. For example, beryllium, magnesium, calcium, strontium, and cadmium all appear in the second column of the short-form table. Not surprisingly, the 8-column table is still used in certain parts of the world, most importantly in Russia where its most successful version was first discovered by Mendeleev in 1869.

The expansion of the periodic table from an 8-column format to one with 18 columns is not essential but seems to have been generally made some years after the initial discovery of chemical periodicity. There are several reasons why this change occurred, some of them scientific and others pragmatic. First of all, it must be recognized that the periodic table is an object of enormous utility that is human-made. It is not given to us directly by nature, even though chemical periodicity is a scientific fact. The precise form of the periodic table that is selected is a compromise that aims to serve the majority of scientists and students of science, but it cannot serve all of them at once. For example, chemists who choose to focus primarily on chemical similarities might wish to favor a different format than chemical educators or experts focusing on atomic structure.

One reason for expanding the table to an 18-column format in this way is that on closer inspection chemical periodicity does not invariably operate with a constant repeat distance of eight elements. If one wants to capture chemical similarities among elements more accurately, one must accept that after two period lengths consisting of eight elements each, the repeat length becomes 18 elements. Consider, for example, the two metals chromium and molybdenum, which are chemically very similar but stand 18 rather than 8 elements apart. The 18-column highlights such similarities more effectively than the short 8-column version.

Another motivation for adopting the 18-column table was that Mendeleev's table displayed certain awkward-looking anomalies. The 8-column table can only truly display chemical periodicity if certain short sequences of elements are excluded from the main body of the table. For example, Mendeleev relegated iron, cobalt, and nickel to what he labeled group VIII (figure 4.4). He did this again for ruthenium, rhodium, and palladium as well as osmium, iridium, and platinum, all of which elements he termed transition elements. In an 18-column table, there is no longer any need to exclude these elements. This feature would seem to suggest that an 18-column format shows some advantages in terms of representing all the elements in an even-handed manner, although as we will see in this, the 18-column table introduces another set of "relegated" elements.

In historical terms, the use of an 18-column format has followed a complicated path. Interestingly, even Mendeleev published some medium-long-form tables, although his versions contained 17 rather than 18 columns since the noble gases had not yet been discovered (figure 4.2).[4] The advent of quantum mechanics and the notion that electrons can be regarded as being situated in distinct shells also seems to have motivated the widespread adoption of a medium-long or 18-column format. Simply put, the 18 groups arise from the fact that, starting with the third main electron shell, electrons occupy s, p, and d orbitals, numbering nine in all, each of which can be doubly occupied to make a total of 18 electrons. Since not all electron shells reach their capacity once they contain 8 electrons, it makes perfect sense to expand the periodic table according to the quantum mechanical explanation of chemical periodicity.

However, as from the fourth electron shell, 14 more electrons can now be accommodated in addition to the previous 18. In modern terminology, we now have f-orbital electrons in addition to the earlier mentioned s-, p-, and d-orbital electrons. To reflect this fact, the periodic table can be expanded further to make it into a 32-column format (figure 1.7). In fact, an increasing number of textbooks are beginning to show such a long-form periodic table, which has both advantages and disadvantages.[5]

On the plus side, the long form allows every single element to be incorporated into the main body of the table. The odd-looking footnote to the 18-column table that traditionally houses the f-block elements now disappears. This is a change analogous to the one that occurs on moving from an 8- to an 18-column format that results in the incorporation of certain otherwise excluded elements into the main body of the table. Returning to the 32-column table, this also shows every single element in its correct sequence in terms of increasing atomic numbers as one moves through each period from left to right. On the downside, presenting the periodic table in a 32-column format requires that the space for each element must be approximately halved. Worse still, the one- or two-letter symbol for each element must now be reduced in size, with the risk of rendering them less legible on the written page or on a wall chart.

What Comes Next?

If we continue to follow this line of thinking regarding the progressive expansion of the periodic table, we notice that the table may be due for yet a further expansion, since rapid advances have taken place in the synthesis of superheavy elements in recent years. The f-block of the table has now been completely filled with elements, the most recent additions being nihonium, moscovium, tennessine, and

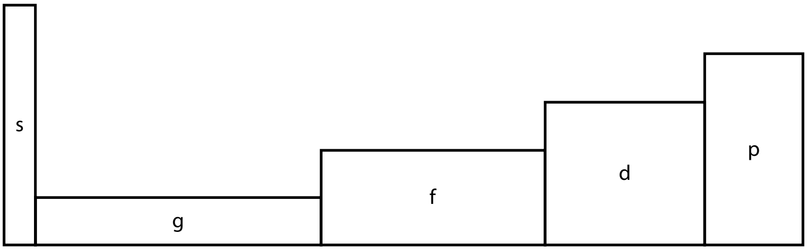


FIGURE 13.1 50-column wide periodic table.

oganesson. For the very first time, and also the last time in the foreseeable future, the periodic table has absolutely no missing gaps, with the current version housing 118 elements arranged in seven periods.

There is no reason to believe that the periodic table has reached its end point, and there are several current initiatives aimed at producing elements 119, 120, and beyond. The discovery of elements 119 and 120 will be easily accommodated by tagging two new spaces directly below francium and radium in either the 18- or 32-column formats. However, as soon as element 121 is synthesized, it will become necessary to introduce a new kind of footnote to the table to house what will be formally known as the g-block elements (figure 13.1). On the other hand, if we insist that all elements be placed together in the main body of the table and that all elements be numbered sequentially, we will have no choice but to introduce a 50-column-wide table (figure 13.1).[6] However, element 121 will only mark the formal beginning of the g-block since theoretical calculations predict that the first element with a true g-orbital electron will occur at approximately element number 125 or so.[7]

Interesting Issues Connected with the Onset of New Blocks of the Table

Each time a new kind of orbital occurs in the sequence of increasing atomic numbers, a new kind of problem also seems to arise. The first time that a d-orbital electron appears is in the atom of scandium, or element 21. In this case, the claim that the atom contains a d-electron is not merely formal but is supported by spectroscopic evidence. The problematical aspect concerns the fact that 3d orbital electrons only begin to appear after the 4s orbital has been occupied in the case of the atoms of potassium and calcium.

As discussed in chapter 9, the vast majority of textbooks state that, in the case of scandium, the final electron enters a 3d orbital. This view immediately creates a problem when it comes to explaining the ionization behavior of the scandium atom. Experimental evidence clearly shows that the 4s electrons are preferentially ionized in scandium. If the 3d orbital had really been the final one to be occupied, it ought to be the first to be ionized, something that runs contrary to the experimental facts. Textbooks typically proceed to fudge the issue, in order to maintain that 4s electrons enter the atom first but are also the first to depart during the ionization process, something that clearly makes no sense in energetic terms.[8]

The problem was clarified relatively recently by the theoretical chemist Eugen Schwarz, who pointed out that in fact the 3d orbital electrons are preferentially occupied in scandium, followed by the 4s electrons, thus explaining why 4s electrons are the first to be ionized.[9] However, there may be a danger in throwing out the "Aufbau baby with the bathwater." Schwarz correctly points out that the Madelung rule fails for all except the s-block elements. This rule that purports to show the relative energies of all the orbitals is part of the staple diet of high school and undergraduate chemistry courses. However, it would be rather unfortunate to dismiss this well-known mnemonic, since it still succeeds in listing the differentiating electron in all but about 20 atoms among the entire periodic table.[10]

As we move through the periodic table, there is no denying that the differentiating electrons in potassium and calcium are 4s electrons, while for scandium, and most of the following transition metal atoms, the differentiating electron occupies a 3d orbital. The Madelung rule is therefore still valid when it comes to discussing the periodic table as a whole, as opposed to the occupation and ionization behavior of a single element such as scandium as discussed above.[11]

First Appearance of an f-Electron

Using the Madelung rule, we find that f-orbital electrons begin to appear in the atom of lanthanum, or element 57. However, according to experimental evidence, this event occurs at the next element cerium ($Z = 58$). Notice how a delayed onset is analogous to the delayed onset of g-electrons as described above.

If one consults current versions of the periodic table, there are at least three versions that are on offer. In the majority of textbooks and wall-chart periodic tables, lanthanum is located in the d-block directly below the atom of yttrium. In a smaller number of currently available periodic tables, one finds that lanthanum is located at the start of a 15-element-wide f-block, and yet a third version places lanthanum at the start of a 14-element-wide f-block.

As a result of these alternative tables, there are three different ways of regarding group 3 of the periodic table. According to the first option, group 3 consists of scandium, yttrium, lanthanum, and actinium (figure 13.2). In the second option, a 15-element-wide f-block, group 3 contains a mere two elements, namely, scandium and yttrium (figure 13.3). Finally, the third form of the periodic table implies that group 3 should be regarded as containing scandium, yttrium, lutetium, and lawrencium (figure 13.4). What is a student of chemistry or even a professional chemist to make of this confusing state of affairs?

Group #

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	**He**
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
Cs	**Ba**	**La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
Fr	**Ra**	**Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Nh**	**Fl**	**Mc**	**Lv**	**Ts**	**Og**

Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

FIGURE 13.2 Medium-long form periodic table based on the version featuring group 3 as Sc, Y, La, and Ac.

Group #

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

FIGURE 13.3 Periodic table published by the International Union for Pure & Applied Chemistry (IUPAC). Group 2 appears to contain only two elements and the lanthanoids and actinoids are 15-columns wide.

Group #

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	**He**
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
Cs	**Ba**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
Fr	**Ra**	**Lr**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Nh**	**Fl**	**Mc**	**Lv**	**Ts**	**Og**

La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**
Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**

FIGURE 13.4 Medium-long form table featuring lutetium and lawrencium in group 3.

A further complication is that neither chemical and physical evidence on the elements concerned, nor microscopic evidence in the form of electronic configurations, provides an unambiguous resolution of the question. One possible way to try to settle the issue is to consider a 32-column table representation of each of these three 18-column tables. Doing so while also maintaining all the elements in their correct sequence of increasing atomic number leads to the elimination of the first option as will be argued later in this chapter.[12]

It is important for IUPAC to recommend a compromise periodic table that most effectively conveys the largest amount of information to the largest group of users.[13] My own personal recommendation is that group 3 should be considered as consisting of scandium, yttrium, lutetium, and lawrencium and that the f-block should formally begin at lanthanum, even though the atom of lanthanum does not actually contain an f-electron. It remains to be seen what the recommendations of the current working group will be on this question.[14]

What does not seem to be well known, even though Jeffrey Leigh has written specifically on the subject, is that there is currently no officially recommended IUPAC periodic table, even though this organization regularly publishes what is purported to be a IUPAC-approved table.[15] Now that the periodic table has reached 150 years, it may be time for IUPAC to recommend one official version.[16]

Periodic Tables Other Than Those Literally Table Shaped

Many representations of the periodic system don't look like tables in the literal sense of having a rectangular shape. For example, there are circular and elliptical periodic systems that serve to highlight the continuity of the elements in a better way than the rectangular forms do. Circular or elliptical systems show no discontinuities at the end of the periods in the way that is implied in the rectangular formats, such as between neon and sodium or between argon and potassium, to cite two examples. But the lengths of periods vary, unlike the periods on a clock face, and as a result, designers of the circular periodic tables need to accommodate the longer periods which contain transition elements. For example, Benfey's table (figure 13.5) achieves this aim by using bulges for the transition metals that point outward from the main circular system. There are also a variety of three-dimensional periodic tables, such as the one designed by Fernando Dufour from Montreal that provides continuous or perhaps pseudocontinuous representations (figure 13.6). Meanwhile, Philip Stewart's periodic galaxy emphasizes the continuity of the elements, unlike the majority of periodic tables that imply breaks in continuity between successive periods (figure 13.7).

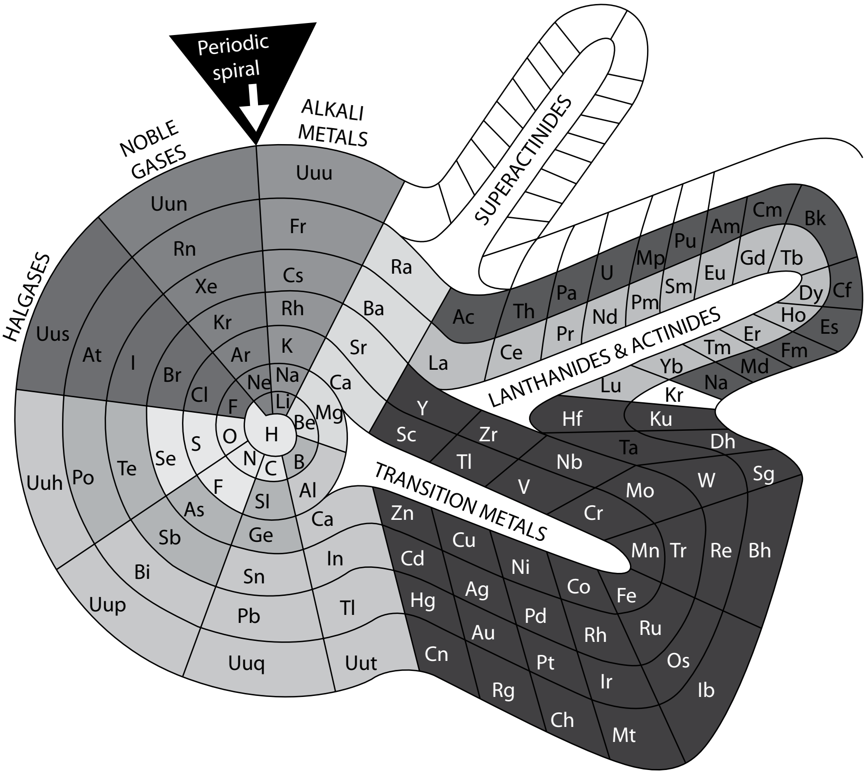


FIGURE 13.5 Benfey's periodic system.

Contributions by Amateurs

The periodic table is a deceptively simple concept, and as a result, it invites amateur scientists to try their hand at developing new versions, which they often claim to have attributes that are superior to all previously published systems. Before dismissing any such attempts, however, one should note that amateurs, or outsiders to the fields of chemistry and physics, have occasionally made major contributions. For example, Anton van den Broek, who was mentioned in chapter 6, was an economist who first came up with the notion of atomic number, an idea that he developed in several journal articles.[17] Van den Broek's work was also the starting point for Moseley's important experimental studies that resulted in the replacement of atomic weight with atomic number as the criterion for ordering the elements.

A second example of a significant contribution from an amateur was that of Charles Janet. He was a French engineer, who in 1929 published the first known

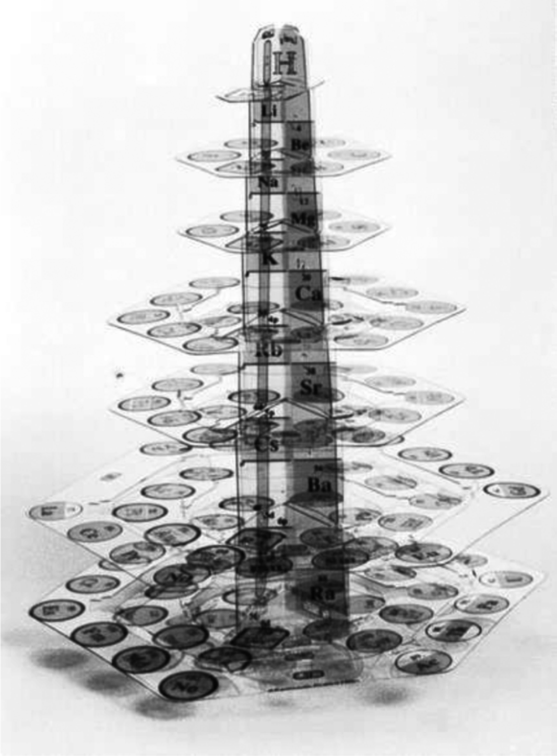


FIGURE 13.6
Dufour's periodic tree.

version of the left-step periodic system, which continues to command much attention among periodic table experts as well as hobbyists (figure 13.8).[18]

More Specific Tables

In 2003, the geologist Bruce Railsback published what he termed "An Earth Scientist's Periodic Table" of the elements and their ions. He claims that such a table arranges lithophiles, siderophiles, and chalcophiles[19] into distinct groups unlike the conventional chemist's periodic table. Railsback also seeks to group elements together into naturally occurring sets, depending on whether they might be concentrated in the mantle, in seawater, or in soil.[20]

Meanwhile, the metallurgist Fathi Habashi has proposed a periodic table in which the element aluminum is moved to the top of the scandium group.[21] To mention another example, the chemist Rayner Canham has published an "Inorganic Chemist's Table" (see figure 13.9), in which he highlights a number of unusual relationships among the elements. One particular feature of his table is the inclusion of the ions CN^- and NH_4^+ because of their similarities to certain elements.[22]

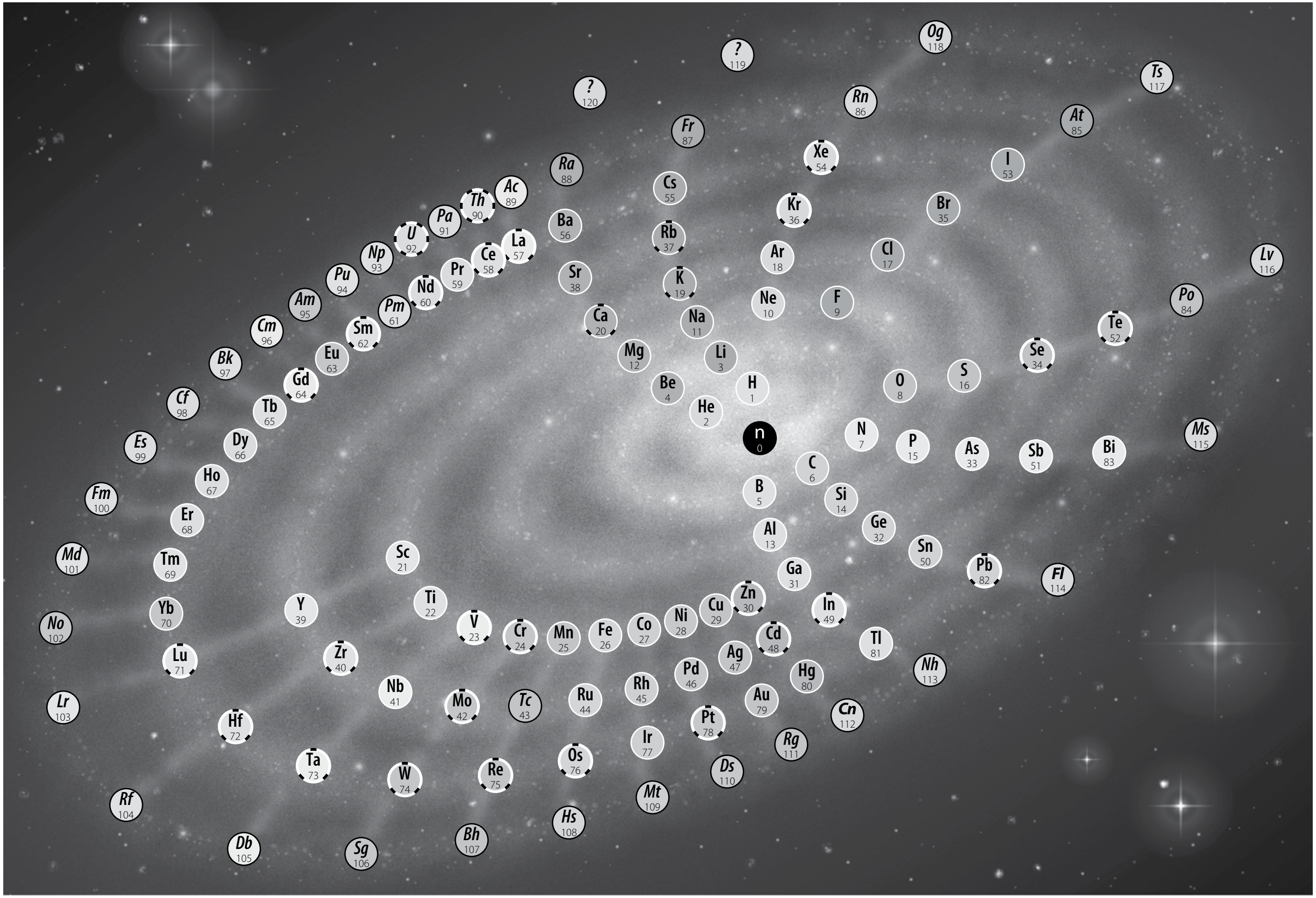


FIGURE 13.7 Philip Stewart’s Chemical Galaxy.

																													H	He
																													Li	Be
																							B	C	N	O	F	Ne	Na	Mg
																							Al	Si	P	S	Cl	Ar	K	Ca
													Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr
													Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra
Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	119	120

FIGURE 13.8 The left-step periodic table due to Charles Janet.

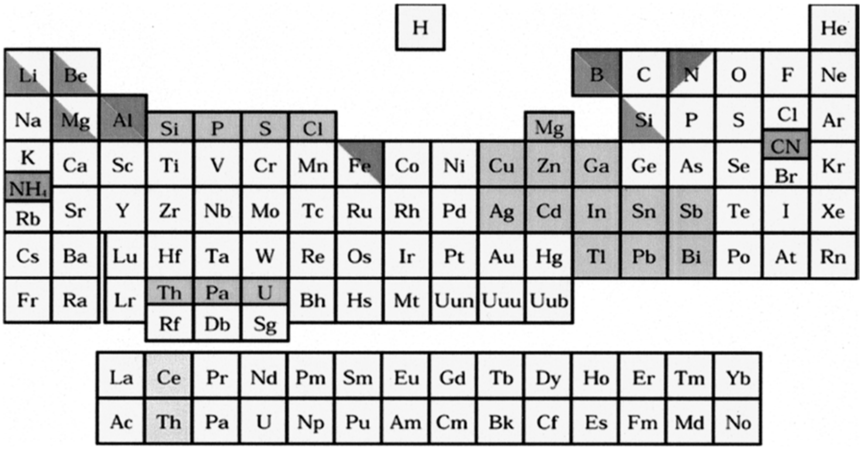


FIGURE 13.9 The inorganic chemist's periodic table, designed by G. Rayner Canham. Shadings indicate relationships: (n) and (n + 10) relationships; diagonal relationships; knight's move relationships; aluminum–iron link; actinoid relationship; lanthanide–actinide relationship; combination elements; pseudoelements.

Is There an Optimal Periodic Table?

Turning to a question that was raised earlier, does it even make sense to seek an optimal periodic table, or are the amateurs deluding themselves along with some expert authors who devote time to this question? I believe that the answer to this question lies in one's philosophical attitude toward the periodic system. If one believes that the approximate repetition in the properties of the elements is an objective fact about the natural world, then one is adopting the attitude of a realist. To such a person, the question of seeking an optimal periodic table does make good sense. To this person, the optimal periodic table is the one that best represents the facts of the matter concerning chemical periodicity, even if an optimal table may not yet have been discovered.

On the other hand, an instrumentalist or antirealist about the periodic table might believe that the periodicity of the elements is a property that is imposed on nature by human agents. If this is the case, there is no particular need to discover *the* optimal table since no such thing would exist. For such a conventionalist or antirealist, it does not matter precisely how the elements are represented since he or she believes that one is dealing with an artificial rather than a natural relationship among the elements.

Just to declare my own position, I am very much a realist when it comes to the periodic table. For example, it surprises me that many chemists take an antirealistic stance concerning the periodic table when asked whether the element hydrogen belongs to group 1 (alkali metals) or group 17 (the halogens). Some other general issues need to be mentioned before examining the details of a possible optimal table. One is the question of the utility of any particular periodic table. Many scientists tend to favor one or other particular form of the periodic table because it may be of greater use to them in their scientific work as an astronomer, geologist, physicist, and so on. These are the tables that are based primarily on utility.

There are other tables that seek to highlight the "truth" about the elements, for want of a better expression, rather than usefulness to any particular scientists. Clearly, any quest for an optimal periodic table should avoid the question of utility, especially if it is utility to one particular scientific discipline or subdiscipline. Moreover, a table that strives for the truth about the elements, above all, will hopefully turn out to be useful to various disciplines if it succeeds in somehow capturing a deeper relationship between the elements. But such usefulness would come as a bonus and should not determine the manner in which the optimal table is arrived at. Said in different words, one can agree that the choice of a particular periodic tale is something of a compromise in terms of what factors are considered, be they electronic, spectroscopic, chemical, or physical. However, one can still strive to find the "best compromise" among the candidate tables being considered.

There is also the question of whether considerations of symmetry should play any role. Many proponents of alternative periodic tables claim that their table is superior because the elements are represented in a more symmetrical, or somehow more elegant, fashion. The question of symmetry and beauty in science has been much debated, but as with all aesthetic questions, what may appear beautiful to one person may not be regarded in the same way by somebody else.[23] One must beware of imposing beauty or regularity on nature where it might not actually be present. Too many proponents of alternative tables seem to argue about the regularity in their representation and forget that they may be talking about the representation and perhaps not the chemical world itself.

Elements and Groups of Elements as Natural Kinds?

Elements defined by their atomic numbers are frequently assumed to represent what philosophers of science call natural kinds.[24] The general idea is that the elements represent the manner in which nature has been "carved at the joints." On this view, the distinction between an element and another one is not a matter of convention. The question arises as to whether groups of elements appearing in the periodic table might also represent such natural kinds. Could it be that some objective feature connects all the elements that share membership to a particular group in the periodic system?

It would seem that the criterion for membership to a group is by no means as clear-cut as that which distinguishes one element from another. In the case of groups of the periodic table, it is the electronic configuration of gas-phase atoms that seems to provide the required criterion, though in neither a necessary nor a sufficient manner.[25] One may also argue that placement of the elements into groups is not a matter of convention. If periodic relationships are objective properties, as I claim here, it would suggest that there is one ideal periodic classification. This in turn would have a bearing on recent questions regarding the placement of some elements within the periodic system. Alternatively, if electronic configurations do not perfectly capture the fact that groups are natural kinds, this may merely indicate the limitations of the concept of electronic configurations.[26]

Some Specific Cases

Having mentioned all these preliminaries, we can delve into some proposed tables, assuming that it does make sense to seek an optimal periodic table. Let us begin with the left-step periodic table, which is one of those substantially different periodic systems in which elements are placed in different groups than in the more conventional tables (figure 13.8). The left-step table was first proposed by Charles Janet, in 1929, shortly after the development of quantum mechanics. However, it seems that Janet's proposal owes nothing to quantum mechanics but was based partly on aesthetic grounds. Yet, it soon became clear that some major features of the left-step table might be more consistent with the quantum mechanical account of atoms than conventional tables are.

First, let us consider how the left-step table is arrived at and how it differs from other periodic tables. The transition from a conventional 32-column table to a left-step periodic table essentially consists of two moves. The left-step table is obtained by moving the element helium from the top of the noble gases (group 18) to the top of the alkaline earth metals (group 2). The two groups of elements on the left of this now modified table are then moved to the right-hand edge to produce the left-step table. Furthermore, if one begins with a conventional 18-column table, the 28-element block that is usually presented as a form of footnote to the periodic table, is now moved to the left side of the new left-step table. As a result, the rare earth elements now become fully incorporated into the periodic table to the left of the transition metal block.

Among the virtues of the left-step table is the fact that the overall shape is more regular and more unified.[27] In addition, we now obtain two very short periods of elements rather than just one as seen in the conventional periodic tables. Instead of the first anomalous period length of two elements that does not repeat, the left-step table features all period lengths repeating once to give a sequence of 2, 2, 8, 8, 18, 18, and so on. None of these advantages involve drawing on quantum mechanics but are, rather, features that Janet seems to have appreciated intuitively. As we have seen in chapter 9, the introduction of quantum mechanics to the periodic table resulted in a deeper understanding based on electronic configurations.

In this approach, the elements in the periodic table differ from each other according to the type of orbital occupied by the differentiating electron.

The overall development of the periodic table is governed by the Madelung or $n + \ell$ rule, even if this rule fails to indicate the order of orbital occupation for any particular element's atom. Adhering to this rule gives the sequence of orbitals shown in figure 9.3. Perhaps the main virtue of the left-step table is the fact that it identifies each new period as a new value of $n + \ell$, as in figure 13.8. Meanwhile, the conventional periodic table identifies each period with a new value of the main quantum number n.

In the conventional tables, the elements in the two leftmost groups are said to form the s-block because their differentiating electrons enter an s orbital. Moving toward the right, we encounter the d-block, then the p-block, and finally the f-block, the last of which appears disconnected under the main body of the conventional table. This order, consisting of the s, d, p orbitals from left to right is not seen as the most "natural" or expected one, since within any given shell the average distance of an electron from the nucleus follows the order

$$s > p > d > f$$

The left-step table, on the other hand, does reproduce this ordering, although it is presented in reverse, reading from left to right.

There may also be another advantage in the left-step table from the quantum mechanical point of view. There is no disputing the fact that the electronic configuration of the helium atom shows two electrons, both of which are in a 1s orbital. This should make helium an s-block element, but in conventional periodic tables helium is placed among the noble gases because of its highly inert chemical properties, just like the remaining noble gases (Ne, Ar, Kr, Xe, Rn).

This situation may be seen as parallel to the earlier historical case of pair reversals such as the case of tellurium and iodine (chapter 5), in which atomic weight ordering had to be ignored in order to preserve chemical similarities. Similarly, in the case of helium, one could argue that electronic structure is not the final arbiter over the placement of elements into groups and that it may be replaced by some new criterion in due course, just as atomic weight was eventually replaced by atomic number in the ordering of the elements. Conversely, this suggested parallel may not hold and electronic configuration may still rule the day, in which case the apparently inert chemistry of helium should be ignored and attention should be placed on its electronic configuration. While the first option favors the conventional periodic table, the second favors the left-step table.

Surprising as it may seem, some chemists have even proposed chemical evidence for placing helium in group 2. Such arguments are based on the first element rule, as discussed above, which states that the first element in any group of the periodic system tends to show several anomalies when compared with successive members of its group. For example, in the p-block, all the first-member elements show a reluctance to expand their octets of outer-shell electrons, while subsequent group members do so quite readily.[28] Another approach that sanctions the removal of helium from the noble gas group lies in recent research suggesting that helium is in fact capable of forming some compounds and that it is not therefore the least reactive of the noble gases. Authors in favor of this view argue that it is neon that is the true first member of the noble gases since it has never been found to form any compounds whatsoever, unlike the remaining members of group 18.[29]

But once again, rather than relying on specific properties of the elements as simple substances, perhaps one should concentrate on elements as basic substances. Such a possibility is discussed below, along with the question of the best possible form for the periodic system.

Back to Elements as Basic Substances

Some preceding chapters discuss the subject of elements as basic substances compared with elements as simple substances. As described in chapter 4, Mendeleev placed greater emphasis on the elements as basic substances than on elements as simple substances when he produced his periodic classification.[30] The main criterion for an element as a basic substance was originally its atomic weight. When atomic number took over the role as the ordering criterion for the elements, Fritz Paneth in particular took it upon himself to redefine the basic substance sense of elements as being characterized by their atomic numbers.[31]

Moreover, in the 1920s, Paneth drew on this sense of elements as basic substances in order to save the periodic system from a major crisis. Over a short period of time, many new isotopes of the elements had been discovered, such that the number of "atoms" or most fundamental units suddenly seemed to have multiplied. The question was whether the periodic system should continue to accommodate the traditionally regarded atoms of each element or whether it would be restructured to accommodate the more elementary isotopes that might now be taken to constitute the true "atoms." Paneth's response was that the periodic system should continue as it had before and accommodate the traditional chemical atoms rather than the individual isotopes of the elements.[32] Paneth regarded isotopes as simple substances in that they are characterized by their atomic weights, while elements as basic substances are characterized by atomic number alone.[33]

Moreover, Paneth, along with György von Hevesy, provided experimental evidence in support of this choice for chemists.[34] They showed that the chemical properties of isotopes of the same element were, for all intents and purposes, identical.[35] As a result, chemists could regard the isotopes of any element as being the same simple substance, even though such atoms might occur in different isotopic forms.

In the case of this isotope controversy, Paneth's recommendation for retention of the chemist's periodic table depended on the notion of elements as basic substances and not as simple substances. If chemists had focused on simple substances, they would have been forced to recognize the new "elements" in the form of isotopes that were being discovered in rapid succession. By choosing to ignore these "elements" in favor of the elements as basic substances, chemists could continue to uphold the idea that the fundamental units of chemistry, or its natural kinds, remained as the entities that occupied a single place in the periodic system.[36] Returning to how the periodic system should be represented, we note that Mendeleev, in particular, favored regarding elements in the more abstract sense, rather than being tied to the elements as being simple or isolated substances.

If one focuses attention on the abstract sense of an element, this could be used to justify moving helium to the alkaline earth group. The concern that helium's chemical lack of reactivity would deny placing it among the more reactive alkaline earths could thus be countered by putting one's attention on an element as an abstract entity rather than as simple substances displaying familiar chemical properties. However, this move amounts to saying "why not" place helium in the alkaline earths if its chemistry can be ignored and cannot therefore be regarded as the final word. A more persuasive argument for moving helium from its traditional position in the periodic table would seem to be needed.

The Placement of Hydrogen in the Periodic System

There has also been considerable debate within chemistry as to placement of the element hydrogen within the periodic system in studies that are completely independent of the validity or otherwise of the left-step table.[37] For example, hydrogen is similar to the alkali metals in its ability to form single positive ions. However, hydrogen can also form single negative ions, thus suggesting that the element might be placed among the halogen elements, which also display this type of ion formation, as occurs in the case of metal hydrides such as NaH and CaH_2.

Can this issue be settled categorically? Some authors allow hydrogen to "float" above the main body of the periodic table; in other words, they do not commit themselves to either one of the possible placements. Peter Atkins and Herbert Kaesz have proposed a modification to the periodic table concerning the placement of the element hydrogen.[38] Contrary to its usual placement at the top of the alkali metals and its occasional placement among the halogens, Atkins and Kaesz choose to position hydrogen on its own, floating above the table. In addition, they place helium alongside hydrogen, thus also removing it from the main body of the periodic table.

Rather than considering the relative virtues of these placements in chemical terms, the argument for removing hydrogen from the main body of the table can be examined from the perspective of the elements as basic substances. The widely held belief among chemists is that the periodic system is a classification of the elements as simple substances that can be isolated and whose properties can be examined experimentally. However, as emphasized in the present book, there is a long-standing philosophical tradition of also regarding the elements as unobservable basic substances.[39]

I suggest that our current inability to place hydrogen in the periodic table in an unambiguous manner should not lead us to exclude it from the periodic law altogether, as Atkins and Kaesz seem to imply. Hydrogen and helium are surely as subject to the periodic law as are all the other elements.[40] Perhaps there is a "fact of the matter" as to the optimum placement of hydrogen and helium in the main body of the table. Perhaps this question is not a matter of utility or convention that can be legislated, as most authors have argued.

The complete removal of hydrogen from the main table seems to be an act of "chemical elitism" since it seems to imply that, whereas all the elements are subject to the periodic law, hydrogen is somehow a special case and as such is above the law.

Group 3 Considered Again

As mentioned earlier, there is also a long-standing dispute among chemists and chemical educators regarding group 3 of the periodic table. Some old periodic tables show the elements in group 3. (See figure 13.2) More recently, periodic tables shown in many textbooks began to show group 3 (figure 13.4), with arguments based on what were once believed to be correct electronic configurations. In 1982, William Jensen of the University of Cincinnati published an influential article in which he argued, that textbook authors and periodic table designers should return to showing group 3 (figure 13.4).[41] Then, even more recently, a rearguard action occurred in which another author argued for a return to Sc, Y, La, Ac.[42]

Nevertheless this proposal has by no means been universally adopted. Many textbooks present group 3 as consisting of scandium, yttrium, lanthanum and actinium as it stood before.

A Historical Survey of Evidence and Arguments in Favor of Placing Lu and Lr into Group 3

Since the advent of quantum mechanics and the precise determination of the electronic configurations of atoms, there has developed a general belief that such an approach should settle any remaining questions having to do with the details of the periodic table. We begin here by discussing evidence based on the electronic configurations of some of the atoms in the question concerning group 3.

Some early determinations on the elements ytterbium (70) and lutetium (71) indicated the following electronic configurations for their atoms.

Yb	[Xe] $4f^{13}$ $5d^1$ $6s^2$
Lu	[Xe] $4f^{14}$ $5d^1$ $6s^2$

As a consequence, it was concluded that lutetium should mark the end of the lanthanide series. In addition, since the discovery of lutetium had taken place at about the same time as the discovery of several other rare earth elements, it was generally thought that lutetium was also a rare earth element.[43]

In 1937, William Meggers and Bourdon Scribner published an article in which they reported that contrary to earlier observations the configuration of ytterbium should be assigned as[44]

Yb [Xe] f^{14} $6s^2$

Nevertheless, the authors did not comment on any possible ramifications for placement of the subsequent element lutetium in the periodic table. If ytterbium possesses 14 f-electrons, rather than 13 as formerly believed, it can genuinely be thought of as the final rare earth element. Consequently, the next element, lutetium, can be regarded as a d-block element, thus placing it under scandium and yttrium in group 3. In the years following this discovery, a few books and published periodic tables incorporated the newly assigned configuration of ytterbium but still refrained from discussing any possible change to the position of lutetium.

The first statement that these configurations provided grounds for regarding lutetium as a d-block rather than as an f-block element comes from the classic book on quantum mechanics by Lev Landau and Evgenii Lifshitz in 1959.[45] The authors stated: "In books on chemistry, lutetium is also placed with the rare earth elements. This, however is incorrect, since the 4f shell is complete in lutetium." This recommended change was then independently rediscovered by a number of other authors, working in different subdisciplines, but none of them seemed to have any impact on the way the periodic table was presented in textbooks or elsewhere, with the possible exception of the work of W.F. Luder.[46] Several of the authors who proposed that lutetium should replace the element lanthanum in group 3 were physicists, a factor that may have contributed to their being ignored by the chemical community.[47]

In 1982, a major development took place in the story of what elements to place in group 3. William Jensen published an article in *Journal of Chemical Education* in which he reviewed previous evidence and made the first concerted plea, to chemists, for periodic tables to be changed so that lutetium would replace lanthanum and lawrencium would replace actinium in group 3.[48] It would seem that this article has not convinced many authors since the majority of periodic tables have remained unchanged and the debate has continued.

Although the article by Jensen represents a major step toward reassignment of the elements lutetium and lawrencium to group 3, the proposal suffers from some limitations that have resulted in its not having the impact that it might have had. While reporting the reassignment of the configuration of ytterbium, Jensen wrote:

> More recent spectroscopic work, however, has revised the earlier electronic configurations (4). Only three of the rare earths in period 6 (La, Gd, and Lu) are now known to have the ground state $[Xe]4f^{x-1}5d^16s^2$, all of the rest having the configuration $[Xe]4f^x6s^2$.... Ytterbium and nobelium should now have configuration [Noble Gas]$(n-2)f^{14}(n-1)d^1ns^2$ resulting in a d rather than an f differentiating electron for both lutetium and lawrencium and making them equally good candidates for the first members of the d-block in periods 6 and 7...both lanthanum and actinium should be considered the last members of the f-block (rather than Lu and Lr), and lutetium and lawrencium (rather than La and Ac) should be considered the first member of the d-block in periods 6 and 7 and assigned to Group IIIB along with scandium and yttrium.

It appears that Jensen did not take the trouble to investigate precisely when the assignment had first been proposed since it was a matter of about 50 years rather than "more recent spectroscopic work." This fact renders it more puzzling that the relocation of lutetium was not seriously considered in earlier times.[49]

The second limitation is that Jensen has been too selective in the evidence he puts forward to support his case (figure 13.10). If other forms of data are appealed to, the case becomes somewhat less compelling.

It should also be mentioned that Jensen was not responsible for assembling this particular data or for presenting it in the fashion shown in his article. As Jensen acknowledges, he was using the data collected and plotted some years earlier by V. M. Christyakov,[50] whose data is somewhat more comprehensive than what Jensen chose to display in his 1982 article.

One may examine how several other properties vary among elements in some transition metal groups. For example, it is not clear why Christyakov, and following him Jensen, chose to focus only on the sum of the first two ionization energies of the elements in question rather than as the sum of the first three ionization energies. The latter quantity is in fact more relevant given the overwhelming tendency of actinides to form ions with a +3 charge.

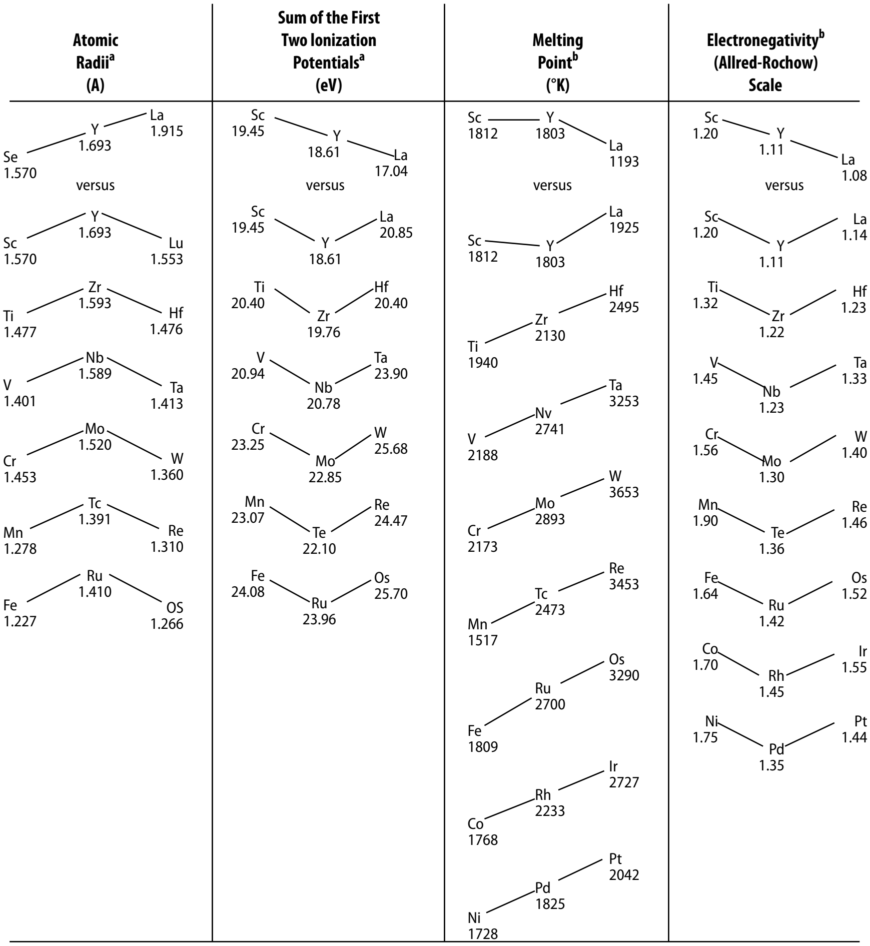


FIGURE 13.10 Jensen's re-presentation of Christyakov's data.

Sum of First Three Ionization Energies

An inspection of figure 13.11 in which the sum of the first three ionization energies is plotted shows that lanthanum fits the general downward trend among transition group elements better than does lutetium. In the case of lutetium, there is a slight increase that appears to be anomalous since none of the other sets of transition metal groups show an increase in the value for the final member of the group, apart from group 12. This feature emphasizes the fact that appealing to specific chemical or physical data on the elements in question is inconclusive.

The data for group 3 metals in figure 13.11 is presented in two ways: first with lanthanum and second with lutetium in place of lanthanum. Lanthanum seems to

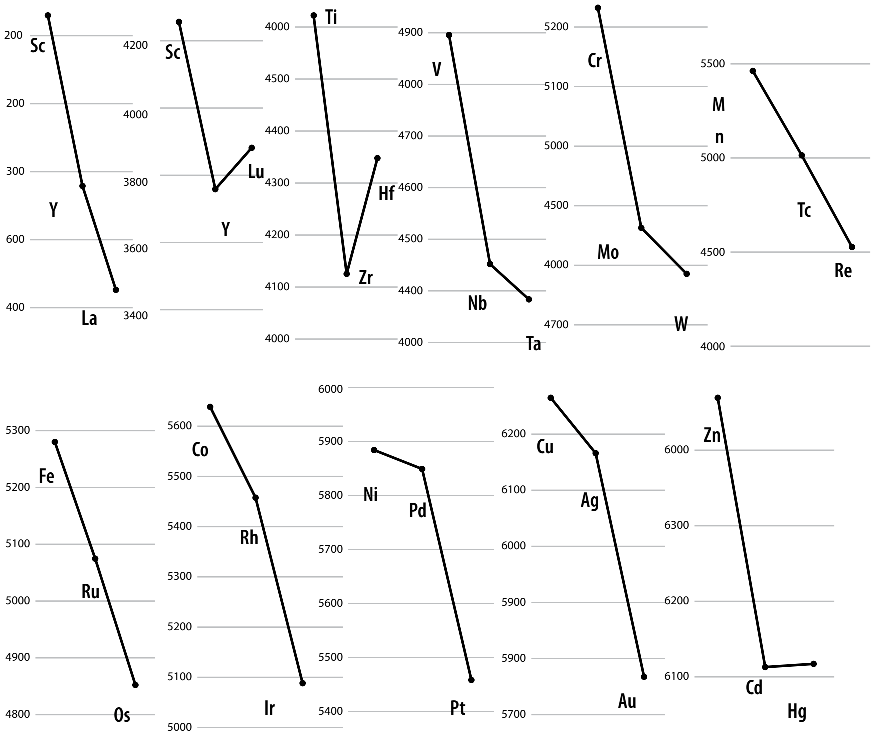


FIGURE 13.11 Sum of first three ionization energies in kJ/mol for first three elements in groups 3 to 12 inclusive. I thank my former UCLA student, William Parsons, for producing these figures.

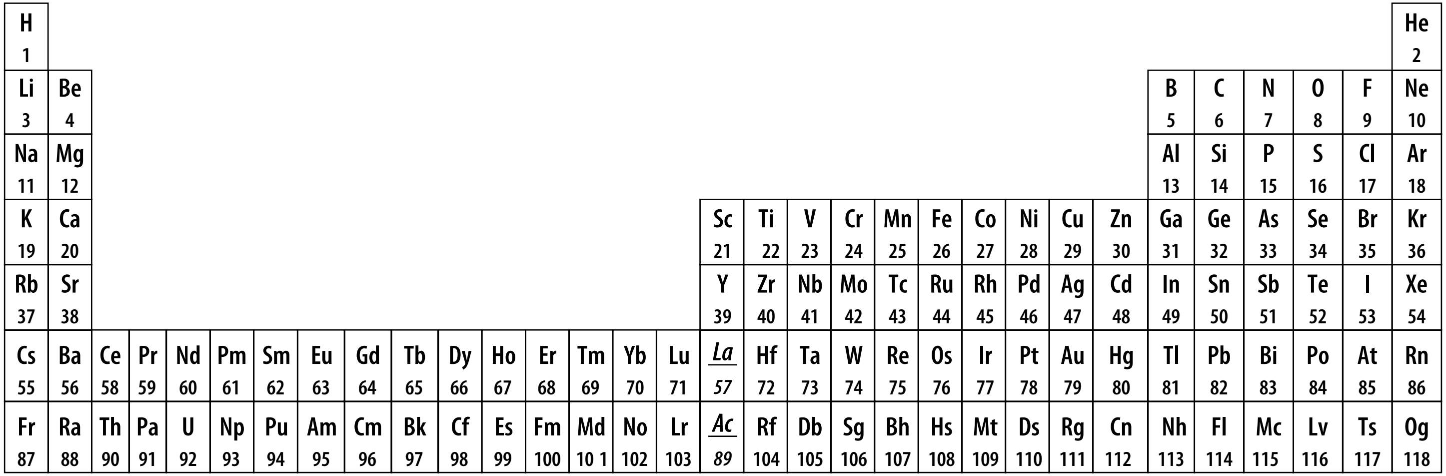
conform to the general downward trend better than lutetium, contrary to Jensen's proposal, thus further underlining the inconclusive nature of arguments based on specific chemical and physical data.

Back to Triads

What bearing, if any, does the notion of atomic number triads have on this group 3 issue? If we consider atomic number triads, the answer is categorical, and Jensen's grouping is favored.

Y	39
Lu	71= (39 + 103)/2
Lr	103

Y	39
La	57 not = (39 + 89)/2 = 64
Ac	89



H 1																															He 2
Li 3	Be 4																									B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20															Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38															Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	*La* *57*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 10 1	No 102	Lr 103	*Ac* *89*	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

FIGURE 13.12 Long-form periodic tables showing lanthanum and actinium below scandium and yttrium in group 3. The sequence of atomic number increase shows two glaring anomalies.

H 1																															He 2
Li 3	Be 4																									B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12																									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20															Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38															Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	*Lu* *71*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	*Lr* *103*	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

FIGURE 13.13 Long-form periodic tables showing alternative placements of Lu and Lr. This version preserves a continuous sequence of atomic number.

H																															He
Li	Be																									B	C	N	O	F	Ne
Na	Mg																									Al	Si	P	S	Cl	Ar
K	Ca	Sc															Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y															Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

FIGURE 13.14 Third option for presenting long-form periodic table in which the d-block is split into two uneven portions of one and nine groups.

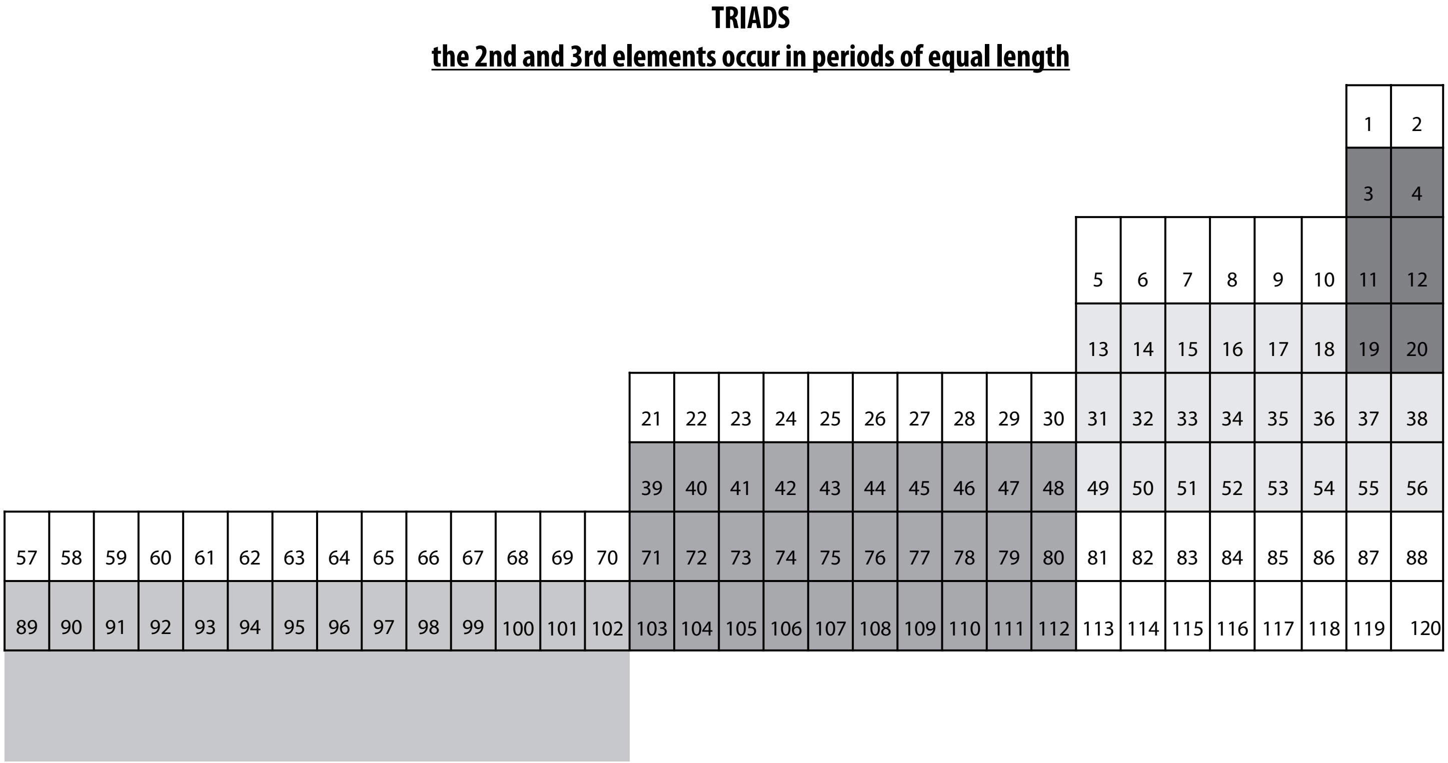


FIGURE 13.15 Triads displayed on a left-step periodic table. All triads have the second and third elements in periods of equal lengths.

There is another reason why regarding group 3 as consisting of Sc, Y, Lu, Lr may be a better option, and this does not depend on any allegiance to atomic number triads.[51]

If we consider the long-form periodic table and attempt to incorporate either lutetium and lawrencium or lanthanum and actinium into group 3, only the first placement makes any sense because it results in a continuously increasing sequence of atomic numbers (figure 13.12). Conversely, the incorporation of lanthanum and actinium into group 3 of a long-form table results in two rather glaring anomalies in terms of sequences of increasing atomic numbers (figure 13.13.)

Finally, there is a third possibility that appears in some textbooks, but one that involves a rather awkward subdivision of the d-block elements as shown in figure 13.14.

Although some books include a periodic table arranged like figure 13.14 it does not seem to be a popular design and for rather obvious reasons. Presenting the periodic table in this fashion requires that the d-block of the periodic table be split up into two highly unequal portions containing one block that is only one element wide and another block that is nine elements wide. Given that this behavior does not occur in any other block in the periodic table, it would appear to be the least likely of the three possible tables to reflect the actual arrangement of the elements in nature. As suggested earlier though, we should beware of arguments based on symmetry and regularity. In addition, there is already one block, or at least the first members of that block, that are generally separated, namely, hydrogen and helium in the s-block. Nevertheless, this splitting of two members of the s-block occurs in an even or 50%–50% fashion, whereas the splitting of the d-block as seen in figure 13.14 is clearly very uneven.

Reductionist Worries

It may seem odd to the reader that the optimal tables under consideration, such as the left-step table, appear to rest rather heavily on a reductionist view in favor of the importance of electronic configurations of atoms. In addition, these considerations, and more specifically the $n + \ell$ rule concerning the order of filling of atomic orbitals, are being placed above the current wisdom concerning the chemical nature of helium, which dictates that it should be regarded as a noble gas par excellence and not as an alkaline earth element.

My response to such worries is to point out that throughout this book I have sought to examine the limits of reductionism in chemistry and have not been critical of reductionism as a general approach.[52] As mentioned at the outset, reductionism has provided an undeniably successful approach to the acquisition of scientific knowledge. The thrust of this book has been directed against exaggerated claims made on behalf of reductionism—for example, Bohr's claim that he had predicted the chemical nature of the element hafnium from first principles or the claim that all aspects of the periodic table have been strictly deduced from the later quantum mechanics. It is the limitations of reductionism, rather than its wholesale rejection, that is of interest to philosophers of science and that should be taken more seriously by science educators.

A Final Word on Triads of Elements

It is interesting to enquire about the conditions under which correct traids of elements occur in the periodic table. In the case of conventional periodic tables that feature the s-block on the left edge of the table something of an anomaly appears.

For s-block elements alone, a triad of elements only occurs if the first and second elements occur in periods of equal lengths as in the case of lithium (3), sodium (11) and potassium (19), However in the case of the p and d-blocks and in principle even the f-block, triads of elements only occur if the second and third elements fall into periods of equal lengths, such as chlorine (17), bromine (35) and iodine (53).

On the other hand, if the elements are presented in the form of a left-step table all triads of elements without exception consists of sets of three elements in which the second and third of them belong to periods of equal lengths (figure 13.15). I now believe that this presents a further and admittedly formal argument in favor of the superiority of the left-step periodic table. It is also my belief that this table may provide the long-sought optimal periodic table.[53]

A Continuum of Periodic Tables?

The philosophical notion of the elements as basic substances and as the bearers of properties was historically important in the case of Mendeleev's establishment of the periodic system and Paneth's resolution of the fate of the periodic system in light of the discovery of isotopes.

I have suggested that the notion of elements as basic substances can cast some light on the question of the optimal representation of the periodic system. As in the case of the distinction between elements as basic substances and as simple substances, the aim should be to obtain a classification that primarily classifies elements as basic substances, while also recognizing aspects of the elements as simple substances. An optimal classification will not be obtained by behaving as naïve inductivists and agonizing over the minutiae of the properties of hydrogen, helium, or other problematic elements. It is suggested that an optimal classification can be obtained by identifying the deepest and most general principles that govern the atoms of the elements, such as the $n + \ell$ rule, and by basing the representation of the elements on such principles.

I conclude with a less controversial proposal. Let us imagine that the various representations of the periodic system lie on a continuum. At one end of this continuum is the "unruly" Rayner Canham table (figure 13.9) that attempts to do justice to many unusual relationships of the kind that are highlighted in chapter 14. At the other end of the continuum lies what I call the Platonic periodic table, or what is usually called the left-step or Janet periodic table[54] (figure 13.8). Somewhere near the middle of this continuum of representations, one can locate the currently popular medium-long representation. It is not altogether surprising that this form has been so persistent since it appears to capture the correct balance between utility and the display of order and regularity. While it sacrifices many of the unusual chemical and physical relationships that Rayner Canham's table features, it embodies the physics and chemistry of the elements as simple substances as well as basic substances. At the same time, the medium-long form stops short of adopting a fully reductionist approach that puts the highest premium on electronic configurations, which would commit one to the placement of helium among the alkaline earths.

The left-step table, I suggest, embodies the elements entirely as basic substances since it relegates the chemical and physical properties of elements such as helium and places greater importance on more fundamental aspects. From a philosophical point of view, I believe that the left-step table may provide an optimal periodic system in showing the greatest degree of regularity, while also adhering to the deepest available principles relating to the elements as basic substances.

It would be gratifying to think that a philosophical version of the periodic table may eventually become the standard form of the periodic system. It is with some trepidation that I advocate the general adoption of the left-step periodic system since I am well aware of the resistance that this proposal will meet, especially from the chemical community, which, rightly or wrongly, regards itself as the sole proprietor of the periodic system.[55]

Notes

1. E. Mazurs, *Graphical Representations of the Periodic System During 100 Years*, University of Alabama Press, Tuscaloosa, 1974.

2. These days the most comprehensive repository of periodic tables in the website was created by Mark Leach, https://www.meta-synthesis.com/webbook/35_pt/pt_database.php

3. E. Scerri, *The Periodic Table, Its Story and Its Significance*, Oxford University Press, New York, 2007.

4. E. Scerri, *A Very Short Introduction to the Periodic Table*, Oxford University Press, New York, 2011.

5. G. Rayner-Canham, T. Overton, *Descriptive Inorganic Chemistry*, 3rd ed., W.H. Freeman, New York, 2002, 18.

6. There is some disagreement regarding the precise form of 50-column tables. P. Pyykko, A Suggested Periodic Table up to Z = 172, Based on Dirac-Fock Calculations on Atoms and Ions, *Chemistry Chemical Physics,* 2011, 13, 161–168; P. Karol, Heavy,

Superheavy…Quo Vadis…in E.R. Scerri, G. Restrepo, *From Mendeleev to Oganesson*, Oxford University Press, New York, 2018, 8–42.

7. P. Pyykkö, Relativistic Effects in Chemistry, *Chemical Reviews,* 88, 563–594, 1988.

8. E. Scerri, The Trouble with the Aufbau Principle, *Education in Chemistry*, 24–26, November, 2013.

9. W.H.E. Schwarz, The Full Story of the Electron Configurations of the Transition Elements, *Journal of Chemical Education,* 87, 444–448, 2010.

10. S. Salehzadeh, F. Maleki, The 4s and 3d Subshells: Which One Fills First in Progressing Through the Periodic Table and Which One Fills First in Any Particular Atom? *Foundations of Chemistry,* 18, 57–65, 2016.

11. Ibid.

12. E.R. Scerri, W. Parsons, What Elements Belong in Group 3 of the Periodic Table? in E. Scerri, G. Restrepo (eds.), *From Mendeleev to Oganesson*, Oxford University Press, New York, 2018, 140–151.

13. At present, there is no official recommendation from IUPAC. The situation may change following the report from the working group charged with looking into the question of group III of the periodic table.

14. Group 3 IUPAC Working Group, https://iupac.org/what-we-do/periodic-table-of-elements/#a7

15. J. Leigh, Periodic Tables and IUPAC, *Chemistry International*, 31 (January–February) 2009, http://old2015.iupac.org/publications/ci/2009/3101/1_leigh.html

16. At the time of writing, the author is the chair of a working group tasked with making recommendations about group III of the periodic table and how this might impact any official IUPAC periodic table.

17. E. Scerri, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016.

18. P.J. Stewart, Charles Janet, Unrecognized Genius of the Periodic System, *Foundations of Chemistry*, 12, 5–15, 2010; E.R. Scerri, Chapter 8, Janet, *A Tale of Seven Scientists and a New Philosophy of Science*, Oxford University Press, New York, 2016.

19. Lithophiles are “rock-loving” elements found predominantly in oxide minerals or as halides. Siderophiles, or “iron-loving” elements, are found mostly in the earth’s core, and chalcophiles are elements found in the earth’s crust in combination with nonmetals, including sulfur, selenium, and arsenic.

20. B. Railsback, An Earth Scientist’s Periodic Table of the Elements and Their Ions, *Geology*, 31, 737–740, 2003.

21. F. Habashi, A New Look at the Periodic Table, *Interdisciplinary Science Reviews*, 22, 53–60, 1997.

22. G. Rayner Canham in The Richness of Periodic Patterns, D. Rouvray, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Research Studies Press, Bristol, UK, 2004, 161–187; G. Rayner Canham, T. Overton, *Descriptive Inorganic Chemistry*, 3rd ed., W.H. Freeman, New York, 2003.

23. J. McAllister, *Beauty and Revolution in Science*, Cornell University Press, Ithaca, NY, 1996. Also see F.T. Marchese, Periodicity, Visualization, and Design, *Foundations of Chemistry*, 15, 31–55, 2013.

24. S. Kripke, Naming and Necessity, in D. Davidson, G. Harman (eds.), *Semantics of Natural Language*, Reidel, Dordrecht, Netherlands, 1972, 253–355; H. Putnam, The Meaning of Meaning, in his *Philosophical Papers*, vol. 2, Cambridge University Press, Cambridge, 1975, 215–271.

25. If the possession of a particular electronic configuration were a necessary condition for membership to a particular group, this would imply that all members of a group have

the same outer-shell configuration. This is violated by many groups of transition elements. If the possession of a particular electronic configuration were a sufficient condition, this would imply that elements with the same outer-shell configuration must be grouped together. This is violated by the case of helium, at least in the conventional representations of the periodic system. E.R. Scerri, How Ab Initio Is Ab Initio Quantum Chemistry? *Foundations of Chemistry*, 6, 93–116, 2004.

26. Electronic configurations are known to be approximations, unlike atomic number, which can be given a clear realistic interpretation in terms of the number of protons in the nucleus of any atom. E.R. Scerri, How Ab Inito Is Ab Initio Quantum Chemistry? *Foundations of Chemistry*, 6, 93–116, 2004.

27. This argument is of course not so compelling, given what was said above concerning symmetry and beauty in science.

28. H.E. Bent, *New Ideas in Chemistry from Fresh Energy for the Periodic Law*, Author House, Bloomington, IN, 2006; N.S. Imyanitov, Spiral as the Fundamental Graphic Representation of the Periodic Law: Blocks of Elements as the Autonomic Parts of the Periodic System, *Foundations of Chemistry*, 18, 153–173, 2016.

29. Anonymous, Helium Succumbs to Pressure, *Nature*, 542, 274–274, 2017; X. Dong et al., A Stable Compound of Helium and Sodium at High Pressure, *Nature Chemistry* 9, 440–445, 2017; W. Grochala, On the Position of Helium and Neon in the Periodic Table of Elements, *Foundations of Chemistry*, 20, 191–207, 2018.

30. Some authors object to the use of the word "substance" in this context because it would seem to imply a form of materiality, especially among physical scientists. To the philosopher, a substance underlies the material aspects or lies below them. This latter sense is the intended one in the discussion of the abstract sense of elements.

31. F.A. Paneth, The Epistemological Status of the Concept of Element, *British Journal for the Philosophy of Science*, 13, 1–14, 144–160, 1962, reprinted in *Foundations of Chemistry*, 5, 113–145, 2003.

32. Another radiochemist, Kasimir Fajans, was Paneth's leading opponent in believing that the periodic system would not survive the discovery of isotopes.

33. F.A. Paneth, The Epistemological Status of the Concept of Element, *British Journal for the Philosophy of Science*, 13, 1–14, 144–160, 1962, reprinted in *Foundations of Chemistry*, 5, 113–145, 2003.

34. Paneth and Hevesy showed that the electrochemical potential from two cells made from different isotopes of the metal bismuth was the same as far as experimental techniques of the day could distinguish. E.R. Scerri, Realism, Reduction and the Intermediate Position, in N. Bhushan, S. Rosenfeld (eds.), *Minds and Molecules*, Oxford University Press, New York, 2000, pp. 51–72.

35. The fact that later research has revealed some differences even in the chemical properties of isotopes does not alter the central issue under discussion.

36. E.R. Scerri, What Is an Element? What Is the Periodic Table? And What Does Quantum Mechanics Contribute to the Question? *Foundations of Chemistry*, 14, 69–81, 2012.

37. M.W. Cronyn, The Proper Place for Hydrogen in the Periodic Table, *Journal of Chemical Education*, 80, 947–951, 2003; L. Sacks, Concerning the Position of Hydrogen in the Periodic Table, *Foundations of Chemistry*, 8, 31–35, 2006; Vladimir M. Petruševski, J. Cvetković, On the "True Position" of Hydrogen in the Periodic Table, *Foundations of Chemistry*, 20, 251–260, 2018.

38. P.W. Atkins, H. Kaesz, The Placement of Hydrogen in Periodic System, *Chemistry International*, 25, 14, 2003; E.R. Scerri, The Placement of Hydrogen in Periodic System, *Chemistry International*, 26, 21–22, 2004.

39. Once again, an element as a basic substance is assumed to have an atomic number but no chemical properties in the usual sense of the term.

40. Sometimes helium is also excluded from the main body of the table and placed alongside hydrogen.

Examples of such tables, in chronological order, include Bayley, 1882, Carnelly, 1886, Hackh, 1914, Bohr, 1922, and von Antropoff, 1925. For diagrams of these tables, see E. Mazurs, *Graphical Representations of the Periodic System During 100 Years*, University of Alabama Press, Tuscaloosa, 1974.

41. W.B. Jensen, The Positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table, *Journal of Chemical Education*, 59, 634–636, 1982.

42. L. Lavelle, Lanthanum (La) and Actinium (Ac) Should Remain in the d-Block, *Journal of Chemical Education*, 85, 1482–1483, 2008.

43. C.H. Evans, *Episodes from the History of the Rare Earth Elements*, Springer, Berlin, 1996.

44. W.F. Meggers, B.F. Scribner, The Arc and Spark Spectra of Ytterbium, *Journal of Research National Bureau of Standards*, 19, 651, 1937.

45. L.D. Landau, E.M. Lifshitz, *Quantum Mechanics*, Pergamon, London, 1959, footnote on p. 245.

46. W. F. Luder, Electron Configuration as the Basis of the Periodic Table, *Journal of Chemical Education,* 20, 21, 1943.

47. D.C. Hamilton, M.A. Jensen, Mechanism for Superconductivity in Lanthanum and Uranium, *Physical Review Letters*, 11, 205, 1963 ; B.T. Matthias, W.H., Zacharisen, G.W. Webb, J.J. Englehardt, Anomalous melting Points of f-Electron Metals, *Physical Review Letters*, 18, 781, 1967.

48. W.B. Jensen, The Positions of Lanthanum(Actinium) and Lutetium(Lawrencium) in the Periodic Table, *Journal of Chemical Education*, 1982, 59, 634–636.

49. Some authors did place lutetium and element 103 in the same group as scandium and yttrium but for quite different reasons. One such example is Charles Janet; see P. Stewart, *Foundations of Chemistry* 12, 5–15, 2010.

50. V.M. Christyakov, *Zhurnal Obshch. Khim.*, 38, 209, 1968.

51. E. Scerri, Mendeleev's Periodic Table Is Finally Completed and What to Do about Group 3? *Chemistry International*, 34, 1–5, 2012.

52. E. Scerri, The Failure of Reduction and How to Resist the Disunity of Science in Chemical Education, *Science and Education*, 9, 405–425, 2000.

53. In the first edition of this book of 2007 I was far less convinced of the value of the left-step table. In the intervening years I also proposed the relocation of the element hydrogen to the halogen group on the basis that this wuld provide a new atomic number triad consisting of hydrogen (1), fluorine (9) and chlorine (17). I now reject this proposal. As figure 13.15 emphasizes, the first members of all groups are not members of any atomic number triads.

54. Charles Janet seems to have been the first author to publish this form of table. C. Janet, The Helicoidal Classification of Elements, *Chemical News*, 138, 372–374, 388–393, 1929.

55. E.R. Scerri, The Tyranny of the Chemist, *Chemistry International*, 28, 11–12, May–June, 2006.

CHAPTER

14

MORE CHEMISTRY

The trends within rows and columns of the periodic table are quite well known and are not repeated here.[1] Instead, I concentrate on a number of other chemical trends, some of which challenge the form of reductionism that attempts to provide explanations based on electronic configurations alone.[2] In the case of one particular trend described here, the knight's move, the chemical behavior defies any theoretical understanding whatsoever, at least at the present time.

Diagonal Behavior

As is well known to students of inorganic chemistry, a small number of elements display what is termed diagonal behavior where, in apparent violation of group trends, two elements from adjacent groups show greater similarity than is observed between these elements and the members of their own respective groups (figure 14.1). Of these three classic examples of diagonal behavior, let us concentrate on the first one to the left in the periodic table, that between lithium and magnesium. The similarities between these two elements are as follows:

1. Whereas the alkali metals form peroxides and superoxides, lithium behaves like a typical alkaline earth in forming only a normal oxide with formula Li_2O.
2. Unlike the other alkali metals, lithium forms a nitride, Li_3N, as do the alkaline earths.

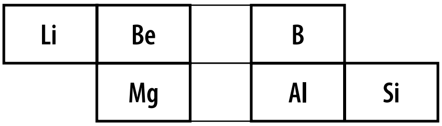


FIGURE 14.1
Elements that display diagonal behavior: lithium and magnesium, beryllium and aluminum, and boron and silicon.

3. Although the salts of most alkali metals are soluble, the carbonate, sulfate, and fluorides of lithium are insoluble, as in the case of the alkaline earth elements.
4. Lithium and magnesium both form organometallic compounds that act as useful reagents in organic chemistry. Lithium typically forms such compounds as $Li(CH_3)_3$, while magnesium forms such compounds as CH_3MgBr, a typical Grignard reagent that is used in nucleophilic addition reactions. Organolithium and organomagnesium compounds are very strong bases that react with water to form alkanes.
5. Lithium salts display considerable covalent character, unlike their alkali metal homologues but in common with many alkaline earth salts.
6. Whereas the carbonates of the alkali metals do not decompose on heating, that of lithium behaves like the carbonates of the alkaline earths in forming the oxide and carbon dioxide gas.
7. Lithium is a considerably harder metal than other alkali metals and similar in hardness to the alkaline earths.

Although some good explanations for this behavior are available, they serve to undermine the simplistic physicist's notion that chemical behavior is governed just by the electronic configuration of atoms.

The diagonal effect can be explained as the outcome of several opposing trends.[3] As one moves down any group, electronegativity, to consider just one property, decreases. But, as one moves across the table, the same quantity increases. If one moves diagonally, the two trends cancel each other out, and there is little change in electronegativity. Similarly, ionization energy and atomic radii trends are such that a diagonal movement results in little change in these properties that, like electronegativity, govern a great deal of the chemistry of the elements. The broader implication is that the electronic configurations of the gas-phase atoms are of little relevance in trying to understand chemical properties. Or to state matters a little differently, the influence of any particular configuration seems to be outweighed by other properties such as those that have just been mentioned, for example, electronegativity and ionization energy.

A rather useful means of discussing the diagonal effect is to appeal to the charge density of the ions of the elements in question, a property that consists of the charge of an ion divided by its volume. The ions of elements that show a diagonal relationship typically have similar charge densities. However, in the case of the boron–silicon relationship, that option is not even available since these elements do not typically form cations.

Similarities Between Group (*n*) and Group (*n* + 10)

The chemical similarities of this type have already been mentioned in passing in chapters 1 and 3. These similarities were well known to the pioneers of the periodic table in the nineteenth century and were embodied in the short-form periodic table (figure 1.6). Unfortunately, many of these trends have been forgotten as a result of the widespread adoption of the medium-long–form table, which does not point to them in any obvious manner.

The first significant example of an *n*, *n* + 10 effect is observed in the elements magnesium and zinc, which belong, respectively, in groups 2 and 12 according to the modern International Union of Pure and Applied Chemistry (IUPAC) numbering scheme. Both elements form water-soluble sulfates and water-insoluble hydroxides as well as carbonates. Also, their chlorides are hygroscopic and predominantly covalent.

Moving one step to the right across the periodic table, one comes to an even more pronounced example of this kind of behavior in the case of aluminum and scandium. In fact, the Canadian chemist and metallurgist Fathi Habashi has suggested that there are grounds for moving the position of aluminum from group 13 into the scandium group or group 3.[4] Indeed, one can even make a good argument for this repositioning on electronic grounds. A comparison of the +3 ions of the elements aluminum, scandium, and gallium suggests that the first two of these elements might be grouped together since they share a noble gas configuration, whereas Ga^{3+} does not.[5]

Some similarities between aluminum and scandium can be seen in figure 14.2. The standard electrode potential for aluminum and the other elements would seem to point clearly in favor of a repositioning to the scandium group. The implications from the melting point data are not quite as suggestive, but it does appear that the high melting-point value of 660°C for aluminum is somewhat anomalous for an element in this group but not so out of place in the scandium group.[6] In addition, both Al^{3+} and Sc^{3+} hydrolyze to produce acidic solutions and contain unusual polymeric hydroxy species. Yet another similarity concerns the reactions of Al^{3+} and Sc^{3+} with hydroxide ions, resulting in the formation of gelatinous precipitates that redissolve in excess hydroxide ions to form such anions as $[Al(OH)_4]^-$. Also, both aluminum and scandium form isomorphous compounds of the general type Na_3MF_6, where M is aluminum or scandium.

Group 3			*Group 13*		
Element	*Melting point (°C)*	*E° (V)*	*Element*	*Melting point (°C)*	*E° (V)*
			Al	660	–1.66
Sc	1,540	–1.88	Ga	30	–0.53
Y	1,500	–2.37	In	160	–0.34
La	920	–2.52	Tl	300	+0.72
Ac	1,050	–2.6	—	—	—

Based on G. Rayner Canham, The Richness of Periodic Patterns, in D. Rouvray, R.B. King, (eds.), *The Periodic Table: Into the 21st Century*, Research Studies Press, Bristol, UK, 2004, 161-187, table on p. 169.

FIGURE 14.2 Comparison of melting points and standard electrode potentials (*E*°) of elements in groups 3 and 13.

Meanwhile, aluminum differs significantly from gallium, the element lying directly below it in group 13. Whereas aluminum forms a polymeric solid hydride with a formula $(AlH_3)x$, gallium forms the gaseous and dimeric hydride Ga_2H_6. Nevertheless, it must also be recognized that the halides of aluminum resemble those of gallium more than they do those of scandium. Nothing is ever simple as far as the elements are concerned.

The case of tin and titanium is interesting for a somewhat different reason (figure 14.3). Here, the similarity is greatest between elements that are related as n and $n + 10$ but that belong to different periods (3 and 4). Moreover, these two elements provide one of the closest similarities between any two elements in different groups, even more so than the classic cases of diagonal relationships mentioned above.

The same kinds of similarities can be seen in cases where $n = 5, 6, 7$, and 8, although not all of these are examined here.[7] The case of groups 8 and 18, for example, is interesting because it is surprising that an element like xenon among the noble gases (group 18 should bear any resemblance to any other elements in the periodic table. And yet both osmium and xenon, from groups 8 and 18, respectively, form covalent compounds in which they show the +8 oxidation state, such as in the cases of OsO_4 and XeO_4, both of which occur as yellow solids. Furthermore, both elements form other sets of analogous compounds, including OsO_2O_4 and XeO_2O_4 as well as OsO_3F_2 and XeO_3F_2.

The only case in which there are no similarities between elements in group n and $n + 10$ are those of group 1 and 11. The alkali metals (group 1) such as sodium and potassium show pronounced *dissimilarities* from such elements as copper, silver, and gold (group 11). The alkali metals are soft, low-density metals that react

Oxides (TiO_2 and SnO_2)

Isomorphous structures

Both show rare property of turning yellow when heated (thermochromism)

Chlorides ($TiCl_4$ and $SnCl_4$)

Similar melting points and boiling points:

$TiCl_4$—melting point, –24°C; boiling point, 136°C

$SnCl_4$—melting point, –33°C; boiling point, 114°C

Both tetrachlorides act as Lewis acids in hydrolysis:

$$TiCl_{4(l)} + 2H_2O_{(l)} \rightarrow TiO_{2(s)} + 4HCl_{(g)}$$

$$SnCl_{4(l)} + 2H_2O_{(l)} \rightarrow SnO_{2(s)} + 4HCl_{(g)}$$

Nitrates of Sn and Ti or $M(NO_3)_4$ are isomorphous

Based on G. Rayner Canham, The Richness of Periodic Patterns, *The Periodic Table: Into the* 21*st Century*, Research Studies Press, Bristol, UK, 2004, 161-187, see p. 170.

FIGURE 14.3 Comparison of titanium (group 4) with tin (group 14).

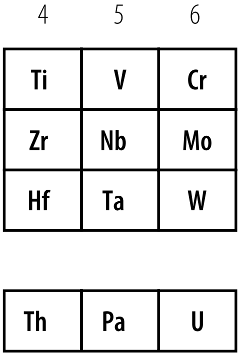
vigorously with water, whereas the so-called noble metals of group 11 are hard, display high density, and, particularly in the legendary case of gold, show great reluctance to react with water and many other reagents.

The fact that these two particular groups should display such an anomaly regarding *n*, *n* + 10 behavior further highlights the complexity of the elements, which, as described here, sometimes defies the reductionist's desire for regimentation. In many of these cases, the reductionist can point to the obvious similarity in electronic configurations between an atom from group *n* and one from group *n* + 10, such as the example of magnesium and zinc discussed earlier. However, as Geoffrey Rayner Canham, a leading advocate of teaching inorganic chemistry in a qualitative manner, has written, the similarities shown far exceed any expectations on electronic grounds.

Early Actinoid Relationships

The relationship concerning members of the actinide series was mentioned in passing in chapter 1. Prior to the work of Glenn Seaborg, the similarities between the transition elements and the early actinides were used to determine the placement of the early actinides in the periodic table (figure 1.9). The modern tendency to separate out the actinides has its merits in terms of electronic configurations but serves, not for the first time, to obscure some undeniable chemical similarities among a number of pairs of elements.[8]

A number of analogies have been noted between thorium and the members of group 4 headed by titanium, between protactinium and members of group 5 headed by vanadium, and between uranium and the members of group 6 headed by chromium (figure 14.4). For example, uranium, which is assigned to the actinide series and is not regarded as a transition metal these days, forms a yellow ion, $U_2O_7^{2-}$, while chromium forms the well-known oxidizing ion with an orange color of formula $Cr_2O_7^{2-}$. The analogy with chromium is further displayed in the compounds UO_2Cl_2 and CrO_2Cl_2, respectively. But in other respects, uranium



4	5	6
Ti	V	Cr
Zr	Nb	Mo
Hf	Ta	W
Th	Pa	U

FIGURE 14.4
Early actinides that show analogies with transition metals. Numbers denote the IUPAC group labels.

resembles tungsten, such as in the formation of the hexachlorides UCl_6 and WCl_6, neither of which is analogously formed by chromium or molybdenum.

Although relativistic effects may well play a role in these matters, they must be outweighed by other factors since these analogies cease quite abruptly beyond group 6, whereas the influence of relativistic effects is known to increase regularly as a function of atomic number. On the other hand, a comparison of the actinides with respective lanthanides lying directly above in the medium-long–form or long-form periodic table reveals little similarity, except for thorium and cerium, in spite of similarities in electronic configurations between members of these two series.

Secondary Periodicity

This behavior was first described in a 25-page paper by the Russian chemist Evgenii Biron. He noted that various chemical and physical properties show a zigzag or alternating behavior instead of the expected regular trend as one descends any group of elements. For example, the elements in group 15 display the zigzag pattern in their common oxidation states, as shown in figure 14.5. Whereas the elements in rows 3 and 5, phosphorus and antimony, show a valence of 5, the other three elements predominantly show trivalence.

The traditional explanation for this behavior has been to invoke the additional electron screening due to the $3d^{10}$ electrons in the case of atoms in row 4, such as arsenic, and the even greater screening in atoms in row 6, such as bismuth. The notion is that whereas phosphorus can readily lose five electrons, at least formally, to form a +5 ion, arsenic cannot do so because of d electron screening, which acts to "separate" the outermost p electrons from the outermost s electrons. A similar argument can be made for the change from antimony to bismuth. The removal of the five outermost electrons in bismuth is prevented by the even greater separation in energy between the 6s and 6p outer-shell electrons due to the intervening $4f^{14}$ electrons, which are absent in the atoms of antimony.[9]

The drop in the sum of the first five ionization energies between arsenic and antimony is at first sight surprising since both sets of outermost p and s electrons are screened to the same extent by 10 d-orbital electrons in each case. But an

Element	Oxidation state	Row	Configuration
Nitrogen	+3	2	[He] $2s^2\ 2p^3$
Phosphorus	+5	3	[Ne] $3s^2\ 3p^3$
Arsenic	+3	4	[Ar] $4s^2\ 3d^{10}\ 4p^3$
Antimony	+5	5	[Kr] $5s^2\ 4d^{10}\ 5p^3$
Bismuth	+3	6	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$

Compiled by the author from E.V. Biron, *Zhurnal Russkogo Fiziko-Khimicheskogo Obschestva, Chast'Khimichevskaya*, 47, 964–988, 1915.

FIGURE 14.5 Secondary periodicity among elements in group 15.

overall decrease in ionization is the normal behavior observed on descending most groups in the periodic table.[10]

Ralph Sanderson, who has published extensively on the periodic system, has listed some further interesting examples of secondary periodicity:[11]

Group 13

B_2H_6 and Ga_2H_6 are volatile, whereas the intervening $(AlH_3)x$ is not.

Stable borohydrides are formed by aluminum but not by boron itself or gallium.

$Al(CH_3)_3$ and $Al(C_2H_5)_3$ are both dimeric in the vapor phase, whereas the analogous boron and gallium compounds are monomeric.

Group 14

Germanium resembles carbon more than silicon does. For example, SiH_4 is far more readily oxidized than is either GeH_4 or CH_4.

Group 15

Phosphorus and antimony form a pentachloride, whereas arsenic does not.

While N(+5) and As(+5) compounds act as good oxidizing agents, P(+5) does not.

N(+3) and As(+3) compounds are far weaker reducing agents than are compounds of P(+3).

Interestingly, secondary periodicity is not confined to main-group elements but occurs even more consistently among transition metals, so much so that this behavior has been used to argue for an alternative placement of lutetium and lawrencium in the periodic table.[12] In 1968, V.M. Christyakov presented data showing that secondary periodicity occurs in most transition metal groups (Figure 14.6).

Group	*Elements (atomic radii)*
3	Sc (1.570), Y (1.693), Lu (1.553)
	La (1.915) is anomalous
4	Ti (1.477), Zr (1.593), Hf (1.476)
5	V (1.401), Nb (1.589), Ta (1.413)
6	Cr (1.453), Mo (1.520), W (1.360)
7	Mn (1.278), Tc (1.391), Re (1.310)
8	Fe (1.227), Ru (1.410), Os (1.266)
11	Cu (1.191), Ag (1.286), Au (1.187)
12	Zn (1.065), Cd (1.184), Hg (1.126)

Table re-drawn from Chistyakov, but using IUPAC group numbering. E.V. Chistyakov, Biron's Secondary Periodicity of the Side d-Subgroups of Mendeleev's Short Table, *Zhurnal Obshchei Khimii* (Engl. Ed.), 38, 213-214, 1968.

FIGURE 14.6 Variation in atomic radii (Å) of free atoms for transition metal groups.

This suggested that the scandium group should consist of scandium, yttrium, and lutetium rather than scandium, yttrium, and lanthanum, as is more frequently assumed in published periodic tables.

Finally, several authors who seek to provide group-theoretical explanations for the periodic system have claimed that their approaches also "predict" secondary periodicity.[13]

Knight's Move Relationship

The knight's move relationship is perhaps the most mysterious one among all the unusual relationships involving the periodic table (figure 14.7). It takes its name from the knight's move in the game of chess, meaning a move of one step in any direction followed by two steps in a direction at right angles to the first movement.[14] The South African chemist Michael Laing discovered such a relationship among the elements[15] and has described it in detail in a number of articles.[16]

The examples of the knight's move relationship so far discovered are located at the heart of the medium-long–form table among metallic elements. Consider the elements zinc and tin. Both are commonly used for plating steel such as in the case of food cans. Not only do layers of both metals successfully delay the onset of corrosion in the iron, but they are also nonpoisonous, unlike many other metals lying close to them in the periodic table.[17] Zinc and tin are not merely nonpoisonous but also appear to be biologically important. Zinc is an essential element for many living organisms because it occurs in a variety of important enzymes. Tin is not essential to humans, although it may be so for some living organisms, a fact that has yet to be settled. The compounds of tin are generally regarded as being nontoxic, with the exception of organotin compounds such as tetramethyltin.[18] Nevertheless, tin is found in many medicines and even in toothpaste in the form of stannous fluoride, which it is claimed can prevent tooth cavities.

Zinc and tin share another important property: their ability to form alloys with the element copper. Whereas they fail to form an alloy with each other and do not form any intermetallic compounds, zinc alloys with copper to form brass and tin alloys with copper to form bronze, both of which have been known since antiquity.[19]

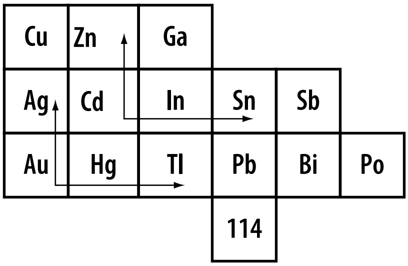


FIGURE 14.7
Elements that show knight's move relationships. For example, zinc and tin, or silver and thallium.

Cadmium and lead, on the other hand, are both poisonous, which is not too surprising when it is realized that they, too, stand in a knight's move relationship to one another. Further similarities include some closely lying boiling and melting points among their chlorides, bromides, and iodides, as shown in figure 14.8. There is also a striking similarity between $PbCrO_4$ and $CdCrO_4$, both of which are yellow substances that are insoluble in water. Figure 14.8 also shows aspects of the knight's move relationship between silver and thallium as well as between gallium and antimony and provides further evidence for the zinc–tin relationship discussed above. The elements silver and thallium form another knight's move pair. Among their similarities is the fact that their monochlorides AgCl and TlCl are both photosensitive and insoluble in water.

Silver and thallium		
AgCl	Melting point	445
TlCl	Melting point	429
AgBr	Melting point	430
TlBr	Melting point	456
Cadmium and lead		
CdI_2	Melting point	385
PbI_2	Melting point	412
$CdCl_2$	Boiling point	980
$PbCl_2$	Boiling point	954
$CdBr_2$	Boiling point	863
$PbBr_2$	Boiling point	916
Zinc and tin		
$ZnCl_2$	Melting point	275
$SnCl_2$	Melting point	247
$ZnBr_2$	Boiling point	650
$SnBr_2$	Boiling point	619
Gallium and antimony		
GaF_3	Melting point	77
SbF_3	Melting point	73
$GaCl_3$	Boiling point	200
$SbCl_3$	Boiling point	221
$GaBr_3$	Boiling point	279
$SbBr_3$	Boiling point	280

Based on M. Laing, The Knight's Move in the Periodic Table *Education in Chemistry*, 36, p. 160-161, 1999, table 1.

FIGURE 14.8 Melting and boiling points that support knight's move relationships among pairs of elements.

Laing has considered possible theoretical explanations of the knight's move relationship but concludes that none is forthcoming. He ends one of his articles by making predictions concerning element 114, which has been observed in trace amounts but has yet to be named.[20] The significance of this element is that it lies in the middle of the so-called island of stability among the superheavy nuclei, which leads one to suppose that it may eventually be possible to synthesize enough of the element to examine its macroscopic properties. Given the knight's move relation to mercury, Laing has predicted that element 114, or eka-lead, should possess a moderate density of around 16 g/cm^3, will have a very low melting point, and will possibly be a liquid at room temperature.[21]

First-Member Anomaly

It has long been recognized that the first members of groups, especially main-group elements, are anomalous with respect to other members of their groups. This applies equally to physical and chemical properties. For example, hydrogen is a gas, unlike the other members of group I. Similarly, nitrogen and oxygen occur as gases at room temperature, whereas all the remaining members of their respective groups are found as solids.

In chemical terms, the first members of each group fail to achieve higher oxidation states; that is, they fail to expand their octet of electrons. For example, oxygen shows a maximum oxidation state of just +2 by contrast to the following members, starting with sulfur, which commonly display oxidation states of +4 and +6. Such behavior in the higher members has usually been explained in electronic terms by invoking available d orbitals that allow the atoms to expand their octets. While nitrogen forms only NCl_3, phosphorus is said to form PCl_5 as a result of promotion of two electrons into available d orbitals and the associated hybridization of the five unpaired electrons. More recently, such explanations have been called into doubt, however. Following some theoretical calculations, it has been argued that the d-orbital contribution to the bonding in compounds in which octet expansion occurs is highly insignificant.[22]

In addition to the kind of first-member anomaly that has just been described, there is a more specific observation that has independently been made by William Jensen and Henry Bent, two inorganic chemists and chemical educators.[23] This effect is such that the extent of the first-member anomaly is greatest in the s-block of the periodic table, followed by a moderate effect in the p-block, and progressively less noticeable in the d- and f-blocks, respectively. Thus, hydrogen is vastly different from its analogues in group 1, namely, the alkali metals, such as sodium and potassium.[24] The first-member anomalies in the case of the p-block elements include the well-known cases mentioned above and involve such elements as nitrogen, oxygen, and fluorine. In the d-block, the first members of each group, such as scandium and titanium, show less pronounced anomalies than the other elements in their groups, and finally in the case of the f-block, the lanthanides show even less difference from the actinides.[25]

But whereas Bent and Jensen have agreed to share the credit for the discovery of this more detailed aspect of the first-member anomaly, they draw surprisingly different conclusions regarding the noble gases. For Jensen, helium remains a noble gas, whereas Bent takes the radical step of moving helium to the alkaline earth group and champions the use of the left-step table.

Other Relationships

Aluminum and iron in their +3 oxidation states show a number of curious similarities. They are especially curious from the point of view of their electronic configurations, which show no hint of any similarity:

Aluminum [Ne] $3s^2 3p^1$ iron [Ar]$4s^2 3d^6$

And yet both of these elements form analogous hydrated ammonium sulfates:

$(NH_4)Al(SO_4)_2{\cdot}12H_2O$ and $(NH_4)Fe(SO_4)_2{\cdot}12H_2O$.

Their chlorides exist as dimers in the gas phase with formulas Al_2Cl_6 and Fe_2Cl_6. Their anhydrous chlorides act as Friedel-Crafts catalysts to introduce alkyl groups into aromatic compounds and contain $AlCl_4^-$ and $FeCl_4^-$, respectively. Finally, the cation of both elements hydrolyzes in water to produce acidic solutions.

Another unexpected behavior consists in the close similarity between the combination of boron and nitrogen in certain compounds and compounds consisting of carbon bonded to itself. First, boron nitride has a structure analogous to graphite. In addition, as in the case of graphite, the application of very high pressure to boron nitride produces an extremely hard substance that behaves like diamond. Even more intriguing is the analogy between the benzene ring with its characteristic aromatic chemistry and the chemistry of the boron–nitrogen analogue consisting of $B_3N_3H_6$, called borazine.[26] A post hoc explanation for these similarities is that the sum of the number of outer electrons in an atom of boron plus those from an atom of nitrogen is eight. Similarly, the total number of outer electrons in two carbon atoms is also eight. One wonders, however, whether such similarities, or others like it, could have been predicted.

Ions That Imitate Elements

There are some examples of polyatomic ions whose behavior mimics that of an ion of a group of elements in the periodic table. This is the case with the ammonium ion, NH_4^+, which in some respects behaves like an alkali metal ion.[27] On the one hand, this may be explained by the remarkable similarity between the charge densities of NH_4^+, which is 151 C/m^3, and K^+ at 152 C/m^3. Nevertheless, the chemistry of the ammonium ion more closely resembles that of Rb^+ and Cs^+. Among the similarities are reactions with the $[Co(NO_2)_6]^{3-}$ anion, which give precipitates in the case of NH_4^+, K^+, Rb^+, and Cs^+.

Superatom Clusters

The recent discovery of superatom clusters threatens to disturb the peaceful order of the periodic table in a radical manner.[28] Some chemical elements present in the form of clusters or "superatoms" can take on the properties of entirely different elements that are completely unrelated in terms of their grouping. Indeed, some cases of a single element can be made to mimic several different elements according to the precise number of atoms present in its cluster. In the 1980s, Thomas Upton at Caltech discovered that a cluster of six aluminum atoms could catalyze the splitting of hydrogen molecules, thus mimicking the behavior of the element ruthenium. Moreover, a superatom consisting of 13 atoms of aluminum behaves as the analogue of noble gas atoms with their full outer shell of electrons. If an electron is removed to form Al_{13}^+, the properties of this superatom ion are similar to those of halogen ions. More specifically, Al_{13}^+ behaves like Br^-. Furthermore, just as Br^- can react with I_2 to form BrI_2^-, the analogous reaction occurs between Al_{13}^+ and I_2 to form $Al_{13}I_2^+$. Even more curiously, a cluster of 14 aluminum atoms mimics the behavior of alkaline earth atoms such as calcium and magnesium.[29] It has been suggested that there might be a new kind of periodic table waiting to be discovered and that the customary two-dimensional table that has been known since the 1860s might require another dimension to take atomic clusters into account.[30]

Notes

1. Readers may wish to consult any of a number of excellent sources on inorganic chemistry, including F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, 1999; N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984.

2. Another unusual relationship, which is not discussed here, is the inert pair effect, whereby the lower members of many groups form stable compounds with a lower oxidation state than do the higher members. E.g., tin and lead form stable dichlorides compared to carbon and silicon, which produce only tetrachlorides. The electrons in the outermost s orbital of the lower members of these groups are said to be inert since they typically do not participate in bonding. A fuller explanation of the inert pair effect requires the application of relativistic quantum mechanics.

3. For further information on the diagonal relationship, see T.P. Hanusa, Reexamining the Diagonal Relationships, *Journal of Chemical Education*, 64, 686–687, 1987.

4. F. Habashi, A New Look at the Periodic Table , *Interdisciplinary Science Reviews*, 22, 53–60, 1997. Also note that IUPAC numbering for groups is used here and in the remainder of this chapter.

5. Ga^{3+} nonetheless shows a closed shell configuration given that the 3d subshell is filled.

6. Nor can the anomalous values for aluminum be attributed to the phenomenon of first-member anomaly for the simple reason that aluminum is the second member of group 13 as matters currently stand.

7. For a fuller discussion of these cases, the reader is referred to the writings of Geoffrey Rayner Canham, which have been drawn on extensively in the writing of this section: G. Rayner Canham, The Richness of Periodic Patterns, in D. Rouvray, R.B. King (eds.), *The Periodic Table: Into the* 21*st Century*, Research Studies Press, Bristol, UK, 2004, 161–187; G. Rayner Canham, T. Overton, *Descriptive Inorganic Chemistry*, 3rd ed., W.H. Freeman, New York, 2003.

8. G.H. Lander, J. Fuger, Actinides: The Unusual World of the 5f Electrons, *Endeavour*, 13, 8–14, 1989.

9. $AsCl_5$ has now actually been prepared, but the difficulty in doing so is shown by the fact that this feat was achieved only in 1977, compared with PCl_5 and $SbCl_5$, which have been known since 1834. On a separate point, the screening explanations have been confirmed by relativistic quantum mechanical calculations carried out by P. Pyykkö, On the Interpretation of "Secondary Periodicity" in the Periodic System, *Journal of Chemical Research* (Sweden), (S), 380–381, 1979.

10. One explanation is that, as the group is descended, the effective nuclear charge (protons minus inner-shell electrons) remains constant, whereas the distance of the outermost electron increases, thus producing an overall decrease in ionization energy.

11. R.T. Sanderson, *Chemical Periodicity*, Reinhold, New York, 1960.

12. E.R. Scerri, Chemistry, Spectroscopy and the Question of Reduction, *Journal of Chemical Education*, 68, 122–126, 1991.

13. H. Obadasi, Some Evidence about the Dynamical Group SO (4,2): Symmetries of the Periodic Table of the Elements, *International Journal of Quantum Chemistry, Symposium* 7, 23–33, 1973; V. Ostrovsky, What and How Physics Contributes to Understanding the Periodic Law, *Foundations of Chemistry*, 3, 145–182, 2001.

14. Of the eight possible knight's moves available in the game of chess, it appears that the chemical knight's move represents just one of these. In all cases, it involves a movement of one step down in the periodic table, followed by two steps to the right.

15. Laing made the discovery of the knight's move relationship in the course of teaching a chemistry course for engineers that caused him to emphasize the similarity between zinc and tin (M. Laing, personal communication).

16. M. Laing, The Knight's Move in the Periodic Table, *Education in Chemistry*, 36, 160–161, November 1999; M. Laing, chapter 4, in D. Rouvray, R.B. King (eds.), Patterns in the Periodic Table, *The Periodic Table: Into the 21st Century*, Research Studies Press, Bristol, UK, 2004, 123–141.

17. E.g., cadmium, which lies directly below zinc, and lead, which lies directly below tin, are both highly toxic. However, cadmium appears to be an essential element for at least one organism, a marine diatom that produces a cadmium-specific enzyme that catalyzes the conversion of carbon dioxide and carbonic acid, as discovered in the year 2000. For further biological information on this element, see J. Emsley, *Nature's Building Blocks*, Oxford University Press, Oxford, 2001, 74–76. This book is the standard reference for the detailed properties of all the elements, including their human, medical, economic, historical, and environmental aspects.

18. Further information on the toxicity of organotin compounds is also to be found in Emsley, *Nature's Building Blocks*.

19. For brass, the earliest regular production appears to date from the fourth century BC or perhaps earlier. From textual sources and actual artifacts, Taxila, in modern Pakistan, has produced the earliest brass, dated from that time. Bronze is far earlier. Copper began to be smelted in the late fifth millennium BC in the Near East. The first copper "alloy" was arsenical copper, where the arsenic had the same useful effect as did tin: hardening the metal, improving the casting quality, and lowering the melting temperature. P.T. Craddock (ed.), 2000 *Years of Zinc and Brass*, British Museum Occasional paper No. 50, London, 1990.

20. M. Laing, The Knight's Move in the Periodic Table, *Education in Chemistry*, 36, 160–161, 1999.

21. More recently, Laing noted even further possible knight's move connections between technetium and iridium (M. Laing, personal communication).

22. L. Suidan, J. Badenhoop, E.D. Glendening, F. Weinhold, Common Textbook and Teaching Misrepresentations of Lewis Structures, *Journal of Chemical Education*, 72, 583–586, 1995.

23. W.B. Jensen, Classification, Symmetry and the Periodic Table, *Computation and Mathematics with Applications*, 12B, 487–510, 1986;

24. I am assuming that hydrogen is indeed placed among the alkali metals, something that has been disputed, for example, by P. Atkins, H. Kaesz, The Placement of Hydrogen in Periodic System, *Chemistry International*, 25, 14–14, 2003. See also a response to this paper: E.R. Scerri, The Placement of Hydrogen in Periodic System, *Chemistry International*, 26, 21–22, 2004.

25. In any case, there are only two elements in each f-block group, which makes it more difficult to establish whether there is any anomaly whatsoever.

26. An excellent and detailed account of boron–nitrogen compounds and their similarities with carbon is given in N.N. Greenwood and A. Earnshaw, *The Chemistry of the Elements*, Pergamon Press, Oxford, 1997, pp. 234–240. The question of whether borazine displays aromatic characteristics is a matter of some debate in the literature. A.K. Phukan, E.D. Jemmis, Is Borazine Aromatic? *Inorganic Chemistry*, 40, 3615–3618, 2001.

27. Another example is the cyanide ion, CN^-, which behaves like a halide ion. See G. Rayner Canham, The Richness of Periodic Patterns, in D. Rouvray, R.B. King (eds.), *The Periodic Table: Into the 21st Century*, Research Studies Press, Bristol, UK, 2004, pp. 161–187. This author goes as far as to include NH_4^+ and CN^- in a newly designed periodic table, a tendency that seems to recapitulate some of the early periodic systems and earlier lists of elements, which also included ions and radicals.

28. P. Jena, Beyond the Periodic Table of Elements: The Role of Superatoms, *Journal of Physical Chemistry Letters,* 4, 1432–1442, 2013.

29. D.E. Bergeron, A.W. Castleman, T. Morisato, S.N. Khanna, The Formation of $Al_{13}I^-$, Evidence for the Superhalogen Character of Al_{13}, *Science*, 231–235, 2004.

30. Anonymous, Evidence That Superatoms Exist Could Unsettle the Periodic Table, *The Economist*, 374, 75, 2005.

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Also see a number of blogs published on the Oxford University blog site, https://blog.oup.com/?s=Scerri and Eric Scerri's website, www.ericscerri.com

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References to tables and figures are denoted by an italicized *t* and *f*.

H 1																															**He** 2
Li 3	**Be** 4																									**B** 5	**C** 6	**N** 7	**O** 8	**F** 9	**Ne** 10
Na 11	**Mg** 12																									**Al** 13	**Si** 14	**P** 15	**S** 16	**Cl** 17	**Ar** 18
K 19	**Ca** 20															**Sc** 21	**Ti** 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	**Se** 34	**Br** 35	**Kr** 36
Rb 37	**Sr** 38															**Y** 39	**Zr** 40	**Nb** 41	**Mo** 42	**Tc** 43	**Ru** 44	**Rh** 45	**Pd** 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	**Te** 52	**I** 53	**Xe** 54
Cs 55	**Ba** 56	**La** 57	**Ce** 58	**Pr** 59	**Nd** 60	**Pm** 61	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71	**Hf** 72	**Ta** 73	**W** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78	**Au** 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	**Po** 84	**At** 85	**Rn** 86
Fr 87	**Ra** 88	**Ac** 89	**Th** 90	**Pa** 91	**U** 92	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

Long-form or 32-column periodic table.

H 1																															**He** 2
Li 3	**Be** 4																									**B** 5	**C** 6	**N** 7	**O** 8	**F** 9	**Ne** 10
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Fr 87	**Ra** 88	**Ac** 89	**Th** 90	**Pa** 91	**U** 92	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

Long-form or 32-column periodic table.