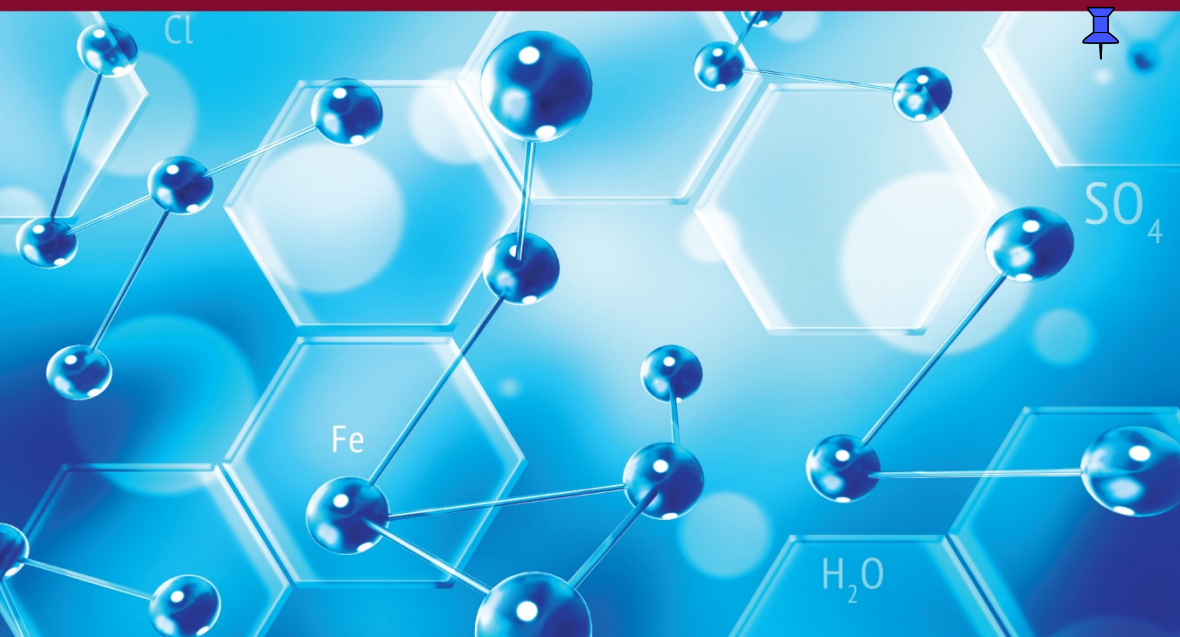


ANALYTICAL AND INORGANIC CHEMISTRY SERIES



Inorganic Chemistry

*From Periodic Classification
to Crystals*

Robert Valls

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Inorganic Chemistry

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From Periodic Classification to Crystals

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First published 2017 in Great Britain and the United States by ISTE Ltd and John Wiley & Sons, Inc.

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ISTE Ltd
27-37 St George's Road
London SW19 4EU
UK

www.iste.co.uk

John Wiley & Sons, Inc.
111 River Street
Hoboken, NJ 07030
USA

www.wiley.com

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Library of Congress Control Number: 2017952433

British Library Cataloguing-in-Publication Data
A CIP record for this book is available from the British Library
ISBN 978-1-78630-254-0

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Acknowledgments

This book has seen the light of day thanks to many students, colleagues and friends who have directly or indirectly contributed to ideas, asked questions and signaled contradictions. But it is within the family that I found the necessary energy, so I particularly thank my wife, Véronique, for her unwavering support throughout the elaboration of this book, her meticulous proofreading and proposals that proved to be always correct and accurate.

I am deeply grateful to my students, who have contributed to my shaping as a chemist as much as I have contributed to their education, and also to my colleagues, teachers and researchers who have always been available for substantive discussions and also for details, and who have helped me with their suggestions, consistently constructive criticism and advice.

I thank Daniel Farran, for his help and concise and clear remarks, as well as for our pleasant and effective discussions.

Many colleagues, students and friends have participated in bringing this book to light. I sincerely thank all of them.

I can only praise VESTA software, without which the project of this book would have been impossible [MOM 11]; as, in my opinion, the quality of representations is essential for clear presentation of structures. Indeed, not everyone has the same 3D visualization performance, therefore rich and clear representation can aid spatial visualization. It is my intention to offer even those who struggle with volume visualization an opportunity to appreciate this field of chemistry.

Those who want to discover or improve their skills in the field are encouraged to use this simple software for a very rapid construction of their own figures, distance measurement, removal of atoms that obstruct the view, exploration of the solid, etc.

The chemist's reference book, Handbook [HAY 15], has been a valuable source of consistent data that can be easily verified by everyone. Many other references have been used and cited, but the fact remains that the Handbook has served as a hub for the choice of data.

Finally, I should mention *Crystallography Open Database* (COD) as a reference in my knowledge-sharing endeavor, thanks to which I could once again offer consistent and easily verifiable data. It is the source of all the examples of simple compounds cited in this book, including the several atypical compounds that illustrate specific properties.

This book aims at making inorganic chemistry known, facilitating its in-depth knowledge or simply its appreciation by means of the periodic table directed toward knowledge of crystals. Above all, I hope to convince the reader to take a different look at this field of chemistry, which is probably not as well-known as it deserves, all the more so as its applications are very frequent and present in our daily life.

Readers who are willing to contribute to the improvement of this book are invited to send me their critical comments and suggestions. I thank them in advance, as I have always received constructive proposals because of which I was able to simplify, clarify or enhance my published works.

Introduction

An Approach to Inorganic Chemistry

Inorganic chemistry mainly involves the study of objects of the mineral kingdom, as opposed to organic chemistry, which obviously deals with organic compounds. Despite the privative prefix seemingly defining as inorganic that which does not retain what is organic, there is no clear demarcation between these two fields of chemistry. As many compounds fall at the boundary between the two fields, there is no clear-cut division between them.

This division can be illustrated as follows: galleries dug by science in the knowledge reservoir throughout its decades-long progress have followed various lodes, and have come to converge despite their starting point being located in distinct areas of knowledge. This may be the characteristic of various branches of chemistry that have converged over time.

According to the most general definition, inorganic chemistry relates to all non-organic compounds formed of elements that compose the periodic table.

One part of this domain may be represented as a list of structures and their corresponding properties, as well as their chemical reactivity, applications and methods used to obtain the elements and their simplest or most complex derivatives.

With this perspective in mind, a presentation can be elaborated depending on the interest that the compounds present for the branch of chemistry practiced by the author. Moreover, presenting all these elements and everything related to them is always a challenge, since, on the one hand, it is

difficult to elaborate an exhaustive presentation, which would come down to plagiarizing encyclopedias, and, on the other hand, it is equally difficult to draw clear limits.

Many books offer these rich and exciting descriptions that make us love chemistry [ANG 07], but this type of description is beyond the scope of the present book.

Given the availability of reliable and comprehensive databases, such as the *Handbook of Chemistry and Physics* [HAY 15], which should always be within our reach, this type of inventory will be omitted here. Moreover, for consistency reasons, that particular work has been used as a source for most of the data in the present book.

Since one of the objectives of this book is to propose easy-to-find and reliable data, links to well-known sites and easy-to-consult files, all accessible to the scientific community, will be provided.

VESTA (*Visualization for Electronic and Structural Analysis*) software has been used for the design of this book, since high quality representation and drawing of the most representative figures may prove to be difficult in the absence of a high performance tool [MOM 11].

All the structures referred to in this book have been taken from Crystallography Open Database (<http://www.crystallography.net/>), a comprehensive resource featuring over 376 000 entries. A number of these structures can be found in the Handbook [HAY 15], in various books or publications, or in other databases that have been consulted for data consolidation purposes.

A brief history reveals that the most ancient branch of inorganic chemistry is unquestionably metallurgy, whose practice dates back to 2500 BC, and is attributed to Egyptians. Indeed, they practiced mining while Europe was in the Bronze Age and Europe's inhabitants began ore mining and processing, making copper and tin alloys.

The Bronze Age was an essential period marked by the use of metals and, above all, by the development of metallurgy and thus the development of the techniques needed for obtaining bronze (an alloy of copper and tin).

Metallurgy is the study of metals: their extraction, properties and processing. By extension, it is also the name given to the industry producing metals and alloys, which relies on the mastering of this science. This emerging metallurgy required expertise in the art of fire, which was acquired by pottery firing. Extraction of metal from ores depends on the mastering of high-temperature furnaces as copper melts at 1085°C, though the melting point can be significantly reduced by the addition of tin. Subsequent to copper metallurgy, iron metallurgy requires a higher temperature as iron melts at 1538°C, which explains the chronology of the bronze and iron ages.

The wealth of empirical knowledge acquired and transmitted gave rise to alchemy, whose fantasies, still present in the collective unconscious, are often associated with chemistry. The best example is the philosopher's stone, which allows for metal transmutation (turning lead into gold, obviously), but alchemists have gone even further and have imagined the panacea (universal remedy), as well as the elixir of life, which nowadays has taken the more mundane name of brandy.

Chemistry as we know it started with the creation of the periodic table, and Lavoisier can be considered its founding father, as he is one of the first experimental chemists.

Referring to the practice and definition of chemistry, Lavoisier stated the following:

“As the usefulness and accuracy of chemistry depends entirely upon the determination of the weights of the ingredients and products both before and after experiments, too much precision cannot be employed in this part of the subject; and, for this purpose, we must be provided with good instruments. As we are often obliged, in chemical processes, to ascertain, within a grain or less, the tare or weight of large and heavy instruments, we must have beams made with peculiar niceness by accurate workmen... I have three sets, of different sizes...

The principle object of chemical experiments is to decompose natural bodies, so as separately to examine the different substances which enter into their composition.” (Antoine-Laurent de Lavoisier, *Elements of Chemistry*, 1789)

These several phrases render both the essential concept, the fact that chemistry is first of all an experimental science, and the fundamental concept, the fact that chemical substances can be decomposed into simple substances. These two notions will lead to the elaboration of the periodic table.

The periodic table has not historically allowed for an explanation of the properties of elements, since it has been in existence for one century, should Moseley be considered the scientist who completed the work. The reverse has actually been the case, as experimentally determined properties of the elements have helped the community of chemists in the 17th Century in the step-by-step building of this currently omnipresent classification.

Inorganic chemistry is the intersection of many branches of chemistry, and this field often leads to crystals and to an understanding of their packing, which may be more or less complex, but is always surprising. Moreover, the set of elements presented in this book should facilitate the comprehension of the structure of perfect crystals (defects will not be covered).

It is thanks to the use of the periodic table, knowledge of the nature of bonds, notions of symmetry and comprehension of binary phase diagrams that crystals are perceived as less enigmatic.

The purpose of this book is to empirically present, based on observations, the structures of the main crystal compounds and to rely on the periodic table for a better comprehension of their structure, linking it whenever possible to the properties of these crystals.

We have therefore opted for a structure in which chapters can be read randomly, the only guide being a need to access data, a desire to immerse oneself once again in a field of knowledge or the opportunity to compare one's knowledge with that presented in the book. This information will be rooted in observations and will be presented in a more empirical rather than theoretical manner, being accompanied by examples and representations that help in visualizing the properties described.

The first chapter presents a reading of the periodic table that relies on the characteristics of atoms and ions (electronegativity, ionization potential, electron binding energy, etc.). It should contribute to an overall original perspective on the periodic table by providing simple and efficient reading keys.

The second chapter develops the bases of crystallography starting from empirical observations and analyses of the structure of metals. It closes with a description of binary phase diagrams that allows the association of structures with properties and offers basic knowledge of metallurgy.

The third chapter offers a presentation of typical crystals depending on the complexity of their chemical formula and of their packing. The study focuses on MX-type binary crystals (CsCl, NaCl, ZnS sphalerite and wurtzite and NiAs) and then on MX₂-type crystals (CaCl₂, Li₂O, TiO₂, CdI₂ and CdCl₂) by means of representations offering descriptions in a simple manner. Finally, it presents ternary perovskite crystals (SrTiO₃) and spinel (MgAl₂O₄).

Visual memory is strongly involved and notions such as ionicity or space availability facilitate a simple and effective approach to the structure and nature of bonds in crystals.

Knowledge of the Periodic Table

1.1. Presentation of the periodic table

The periodic table is one of the chemist's everyday tools for retrieving the properties of an element based on its position in this table and the various values associated with it. However, before proceeding to use it, knowledge of several simple keys and of their limits should be acquired and their operation should be mastered.

This table should not be perceived as a visionary anticipation or thought of as being received by a scientist through revelation. It is the result of lengthy and patient efforts sustained by Mendeleev and all the chemists in his time, drawing on the empirical knowledge accumulated throughout the 18th and 19th Centuries by several generations of chemists engaged in the pursuit of this classification, which was supposed to name and organize all the elements. Dozens of scientists should be cited, but in order to keep the presentation simple, only three of them will be mentioned here, namely those whose interventions were essential. The first one was Lavoisier, who in 1789 had formalized the notion of elements, then came Mendeleev, who is recognized as the creator of the periodic table according to his work published in 1869, and finally Moseley, who in 1913 offered the key to the complete form of the periodic table.

The use of the table in the absence of several reading keys may prove discouraging, as it requires great memory and leaves the impression of a series of successive specific cases. Moreover, the method used by chemists

in order to memorize the periodic table should differ from the one employed for multiplication tables (it is less mechanical), similar to that applied for memorizing the names, location and characteristics of places encountered every day and which are part of real-life experience, therefore involving affective rather than mechanical memorization.

Resorting to deductive presentations of the periodic table does not simplify its acquisition, since the table, though following nearly mathematical laws for some characteristics of the elements, represents a synthesis of all the diversity of nature when it comes to other characteristics.

1.2. Construction of the periodic table

1.2.1. History

In order to allow for a better grasp of the subject, a brief history of the periodic table will be presented, covering five periods that are in our opinion decisive for its elaboration, and whose landmarks are given by the following three important names: Lavoisier, Mendeleev and Moseley.

In the period from Antiquity to the Renaissance, seven metals were known: gold, silver, mercury, copper, iron, lead and tin, as well as several other elements such as sulfur, antimony, arsenic, carbon and phosphorus. By the end of the 17th Century, only these 12 simple substances had been discovered.

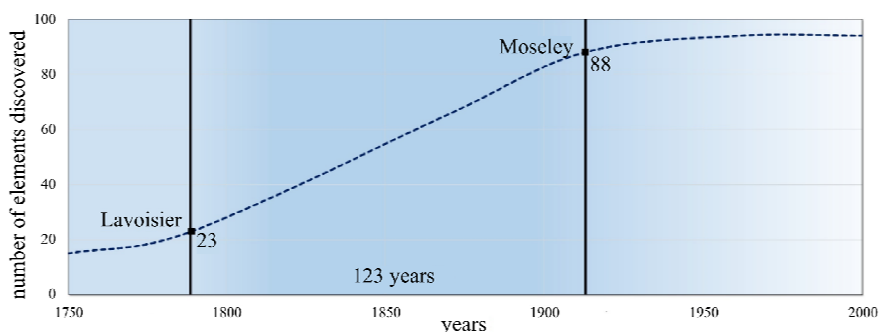


Figure 1.1. Discovery of elements throughout the centuries

As the techniques used for analysis evolved, Lavoisier had 23 elements at the beginning of his research work, but their number rapidly increased, so that in 1869 Mendeleev gathered 65 elements in an arrangement that he proposed as the first classification, and then in 1913 Moseley gave the final form of the current periodic table, which contained 88 elements (see Figure 1.1).

1.2.1.1. *The pioneer: Antoine-Laurent de Lavoisier*

In 1789 Lavoisier (1743–1794), with his *Elements of chemistry*, revolutionized (an action fit for those times) chemistry, being the first to propose a distinction between simple and compound substances. He also advanced the idea that certain chemical products, which cannot be decomposed, should be considered elements. It is safe to consider him the founding father of modern chemistry, given his systematic use of weighing instruments. Moreover, he set the bases of chemistry in the following terms:

“To solve these two questions, it is necessary to be previously acquainted with the analysis of the fermentable substance, and of the products of the fermentation. We may lay it down as an incontestable axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combination of these elements. Upon this principle the whole art of performing chemical experiments depends: We must always suppose an exact equality between the elements of the body examined and those of the products of its analysis.” (Antoine-Laurent de Lavoisier, *Elements of Chemistry*, 1789)

A very reductionist but quite effective variant of the above fragment is often stated as follows: *Nothing is created, nothing is lost, everything is transformed*. Lavoisier proposed the idea of simple substances (elements), while he was still far from the periodic table, but he gradually created a ranking (see Table 1.1).

Lavoisier and Guyton Morveau had therefore at their disposal the first 23 elements indicated in Figure 1.2, which are the starting point for the quest to discover new natural elements and classify them, an endeavor in which many scientists have participated.

1.2.1.2. *The creator: Dmitri Ivanovich Mendeleev*

Eighty years later, in 1869, in his paper entitled *On the correlation of the Properties and Atomic Weights of the Elements*, Mendeleev (1834–1907) set the bases of the current periodic table.

He proposed 42 additional elements, reaching therefore a total of 65 available elements and predicted the existence of missing elements (eka-boron, eka-silicon, eka-aluminum and eka-manganese) together with some of their properties.

On 6 March 1869, Mendeleev presented his work at the meeting of the Russian Chemical Society. The following paragraphs of this presentation are, in our opinion, essential:

“Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g. Pt, Ir, Os) or which increase regularly (e.g. K, Rb, Cs).

The arrangement of the elements or of groups of elements in the order of their atomic weights corresponds with their so-called valences.

The elements which are the most widely distributed in nature have small atomic weights, and all the elements of small atomic weight are characterized by sharply defined properties. They are therefore typical elements. The magnitude of the atomic weight determines the character of an element.

The discovery of many as yet unknown elements may be expected. For instance, elements analogous to aluminum and silicon, whose atomic weights would be between 65 and 75.

He evidenced a strong correlation between the X-ray spectrum (see Figure 1.4) of the elements and their location in the periodic table. It was the confirmation of the modern classification, and, considering the 23 additional elements, a number of 88 elements were reached.

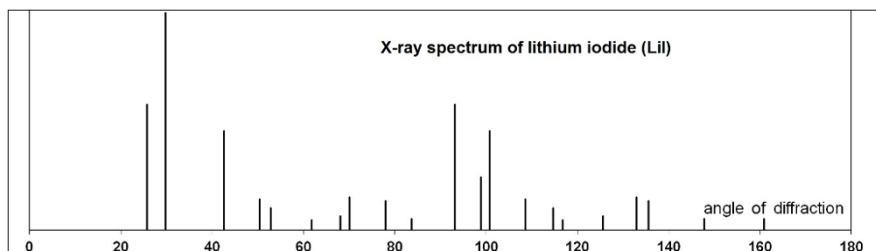


Figure 1.4. X-ray spectrum of lithium iodide

To summarize, the first 23 elements were proposed by Lavoisier, then 124 years later the last 23 elements were added, which led in the end to 88 natural elements, which was completed by the last 6 elements (promethium, technetium, francium, astatine, neptunium and plutonium), which are radionuclides produced in laboratories before having been discovered in nature.

The classification was complete and the position of elements was clearly defined; therefore by 1940 the journey was considered completed, after the synthesis of astatine, neptunium and plutonium.

A last development was triggered due to promethium, which had not really been produced and characterized until 1945.

Ninety-four elements have by now been identified in the Earth's crust, some of which have a history that is difficult to summarize, as information on whether the element has been used, predicted, identified, isolated, synthesized or discovered in nature should be provided, as in the case of technetium (43rd element), which has generated considerable interest and whose history is detailed as a note in the paragraph below.

NOTE 1.1.– The difficulty entailed by summarizing the history of elements can be illustrated by a four-stage description of the discovery of element 43:

1) Mendeleev predicted the properties of element 43, which he named eka-manganese. Its place in the classification between molybdenum and ruthenium suggested that it would be an easy-to-discover element.

2) It was erroneously supposed to be present in a platinum alloy in 1828; it was identified in 1846 (but it proved to be niobium), then in 1877 (a mixture of iridium, rhodium and iron), in 1896 (but it was yttrium), in 1908 (it was rhenium), and in 1925 its existence was effectively proved, but the experiment could not be replicated.

The discovery of technetium (43) was finally attributed to Carlo Perrier and Emilio Segrè who isolated the technetium-97 isotope in 1937 (as its name indicates, it was the first element to have been artificially produced).

3) Technetium was detected in red giants in 1952, and its discovery proved that stars could produce heavy elements during nucleosynthesis.

4) On Earth, technetium was isolated in the form of traces in the uranium ore in 1962 [KEN 62].

The difficulty raised by associating a date to this 43rd element is clear, since it was successively predicted, produced, detected and isolated from the natural environment.

The final, though temporary, point of this quest was perhaps the discovery [KEN 62] in the pitchblende (uranium ore) of traces of neptunium, plutonium and technetium.

Since 94 natural elements were isolated in the Earth's crust, there is no necessity to explain the absence of technetium on Earth, and it can be concluded that all natural elements have been obtained.

Resuming the numbering of Newlands' groups [NEW 65] with Roman numerals from I to VIII (law of octaves), Moseley introduced letters A and B, which have been used until the 20th Century. Columns are currently

nickel arsenide, 135, 185
 noble gases, 10, 13, 14, 16, 17, 20,
 27, 28, 32–34
 non-close-packed, 60, 61, 66, 67, 73
 nucleus, 6, 25–27, 32, 42–45, 48

O, P, R

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 186, 231, 232, 233
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 204, 208

S, T, V, Z

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