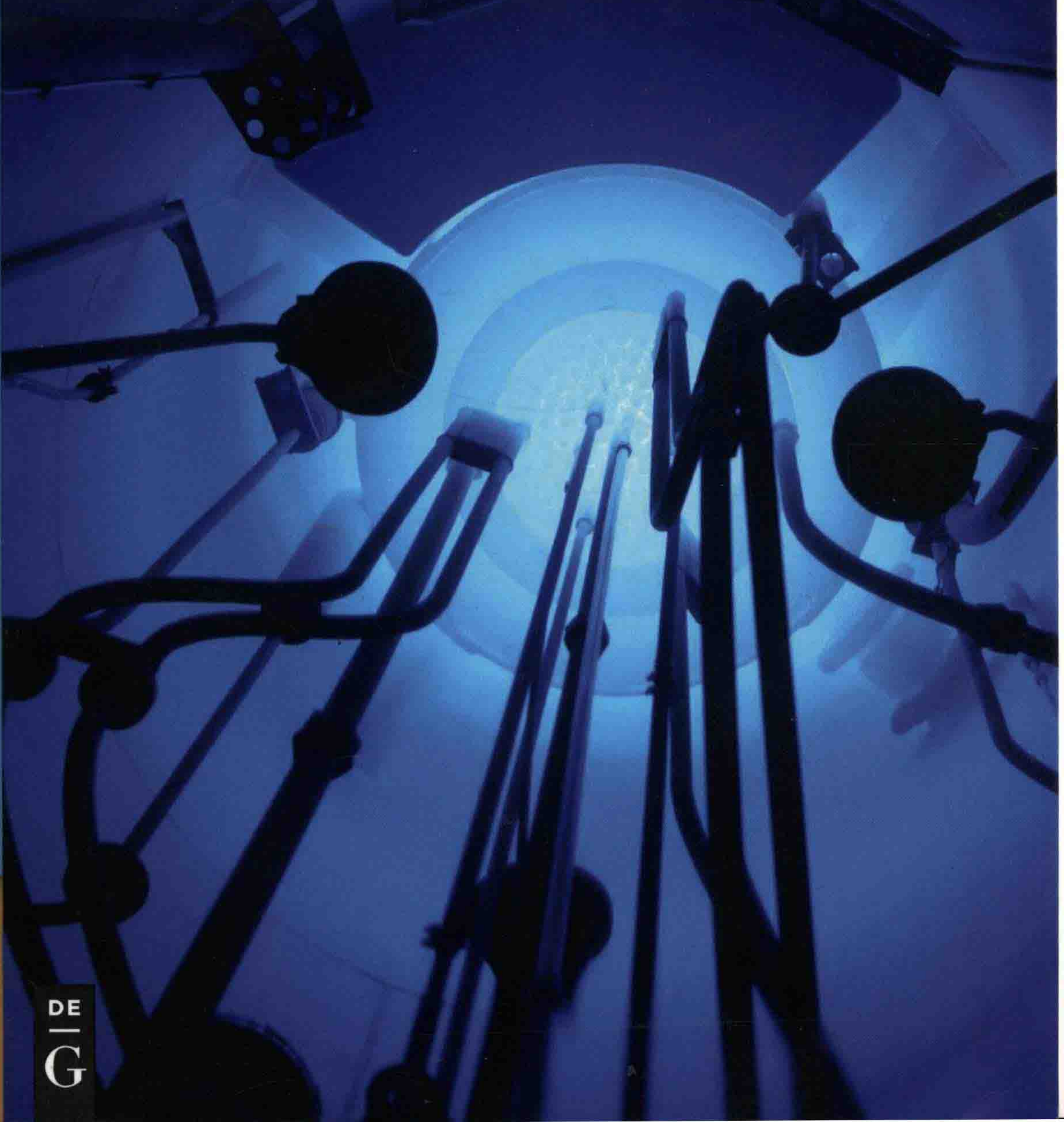
DE GRUYTER GRADUATE

Frank Rösch

NUCLEAR- AND RADIOCHEMISTRY

VOLUME 1: INTRODUCTION



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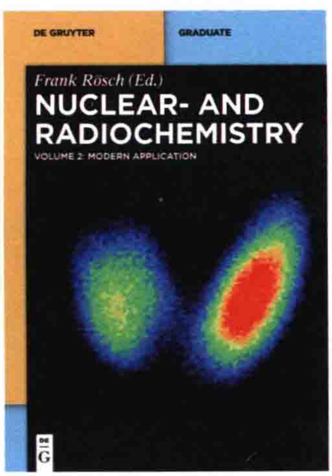

Volume 2:
Modern Applications

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Preface

Except for the element hydrogen with its most common stable isotope ^{1}H, the nuclei of all atoms consist of mixtures of protons and neutrons.[1] For certain, well-defined nucleon compositions (i.e. protons + neutrons), nuclei are stable – they exist forever. This holds true for one or more nuclei of the isotopes of almost all chemical elements (except technetium, Z = 43) ranging from hydrogen (Z = 1) to bismuth (Z = 83). Yet, there are less than 300 stable nuclei altogether.

In contrast, all the elements beyond bismuth (i.e. from Z = 84 to Z = 119) identified so far, and very many isotopes of the lighter elements with stable isotopes (i.e. ranging from Z = 1 to Z = 83) have isotopes comprising nuclei of nucleon compositions not suitable to stability. This means that there are more than 3000 unstable nuclei that must transform into new nuclei of more stable nucleon compositions. This textbook is about the many atomic nuclei, K, and their characteristic states that form the atoms our physical world is made of: stable nuclei (K), nuclei with excited nuclear levels ($^{\circ}K$), unstable nuclei ($^{*}K$), nuclei at ground state (^{g}K) or metastable states (^{m}K).[2]

These transformations proceed in an exothermic way. The velocity of a transformation is expressed by a transformation constant and/or half-life.

The transformation itself is accompanied by the release of various kinds of emissions. It is the velocities of these transformations and it is these emissions that stand for the phenomenon of "radioactivity".

The understanding of basic nuclear and radiochemical processes is a prerequisite to exploring the potential of radionuclides and radioactivity as a source of energy, as tools in fundamental research and analytics, for environmental purposes, for industrial applications, in medicine etc. For example, nuclear fission is one of the most important sources of electricity, while the beta transformation and alpha-emission processes are the essence of several molecular imaging processes adopted in diagnostic nuclear medicine and for patient treatments, respectively. These and several other topics are addressed in the second volume of this textbook.

This first volume of this textbook introduces the basic aspects of these processes. The focus is on the explanation of fundamental aspects rather than on specific details and mathematical treatments. Mathematics and in particular (quantum) physical models are referred to only when they are needed to help to accept experimentally proven effects in radioactive transformations that are unexplainable by conventional physics.

Thus, this textbook serves as a guide to qualitatively understand the essence of radioactivity, treating questions such as:
- Why is a nucleus of an atom stable and why not?
- What is the "motivation" of an unstable nucleus to transform?
- What are the velocities of the transformations?

1 For ^{1}H it is just one single proton.
2 K = Kern (German for "nucleus")

- What are the different primary options to transform?
- What is the rationale of each option?
- What are the consequences of primary transformation routes in terms of secondary pathways and post-effects?
- How is a particular pathway explained by both experimental evidence and theoretical models?
- What are the main properties of the various emissions (the "radiation") released in the course of a transformation?
- How are characteristic emission parameters adopted for the many different practical applications of certain radionuclides, making them valuable tools in research, and industrial and medical fields?
- And finally, how can some of the particularly important radionuclides be produced artificially?

The intention of this textbook is to illuminate the concepts of radioactive transformations. Excellent textbooks on nuclear and particle physics and quantum mechanics are available for more detailed discussions of many of the phenomena. For a comprehensive description of specific aspects of nuclear- and radiochemistry, the six volume, over 3000 page "Handbook of Nuclear Chemistry", A Vértes, S Nagy, Z Klencsár, RG Lovas, F Roesch (eds.), second edition, Springer, 2011, can be recommended. Thus, this textbook may be useful for bachelor students who are interested in nuclear sciences, in radio- and nuclear chemistry, in radiopharmaceutical chemistry, in nuclear analytics, in nuclear energy, but also in nuclear medicine.

The textbook also may assist the many professionals working in the latter field (chemists, physicists, physicians, medical-technical assistants), handling an increasing number and increasing radioactivities of radionuclides in diagnostic and therapeutic nuclear medicine.

About the cover image

The core of the TRIGA research reactor of the Institute of Nuclear Chemistry, Johannes Gutenberg University, Mainz, Germany. The blue light emitted from the fuel elements is CHERENKOV radiation. It is observed at this research reactor in the course of a pulse mode. While the typical neutron flux is 10^{12} n cm^{-2} s^{-1}, the fast removal of one control rod leads to a prompt increase in the nuclear fission rate resulting in a peak neutron flux of up to 10^{15} n cm^{-2} per pulse. Since at increased temperature the special fuel composition of 20 % of ^{235}U embedded in a zirconium(II) hydride matrix ceases to moderate the kinetic energy of the neutrons emitted, it inherently terminates the nuclear fission process. Because this happens within only 0.0025 seconds, the operation mode is called “pulse”.

For induced nuclear fission cf. Chapter 10 on “Spontaneous fission” of this volume, but also Chapter 11 of Volume II on “Nuclear energy”. The neutrons released are used to induce nuclear processes, cf. Chapter 13 on “Nuclear reactions”, but themselves become the subject of research on the properties of the neutron, cf. Chapter 2 on “The atom’s structure II: Nucleus and nucleons”.

The nuclear reaction fission products are neutron rich and transform *via* the primary β^--pathway, cf. Chapter 8 on “β-transformations II: β^--process, β^+-process and electron capture”, releasing β^--particles and antineutrinos, cf. Chapter 7 on “β-transformations I: Elementary particles”.

Contents

1 The atom's structure I: Electrons and shells

Aim: The concept of atoms as the ultimate smallest, not further divisible constituent of matter is introduced. It arises from more than two millennia old Greek philosophy, reaches the atom's renaissance in the 19th century, and reflects the dramatic improvements achieved at the beginning of the 20th century.

Atoms are made of electrons, which exist in the shell of an atom, and a set of different particles located in the atom's nucleus. To understand the chemical properties of an atom, the electron shell structure, i.e. the number and the characteristics of electrons in various shells and the transition of electrons between shells, is essential. To a large extent, this understanding needs a significant reflection on quantum physics.

Developments of concepts of ancient and modern atom theory are introduced, turning from the atomic philosophy of being the ultimate particle to concepts on the atom being a substance of various, subatomic particles. The latter ideas are illustrated as a scientific need to understand pioneering experiments in chemistry and physics, i.e. to correlate experimental evidence and subsequent theoretical explanation.

The latter is meant too to serve as an introduction to quite similar considerations relevant to the structure of nucleons in the atomic nucleus.

1.1 The philosophy of atoms

1.1.1 The beginning: Just philosophy

The concept of an atom was approached about 24 centuries ago, when Aristotle (384–322 BC) suggested that all existing matter is built of four components, namely air, water, fire and earth. Plato (427–347 BC) added a fifth element, the ether, as the one to allow interaction and transformation between the others. The five Platonic solids are illustrated in Fig. 1.1. Interestingly, they are each composed of just one of only three single abstract geometric figures (equilateral triangle, square and a regular pentagon), which when assembled form the tetrahedron, the hexahedron, the octahedron, the icosahedron and the additional one, the dodecahedron.

Almost at the same time, the Greek philosopher Leucippus (ca. 450–370 BC) and his scholar Democritus (460–371 BC) proposed a material world made of indivisible components. Assuming that every material could be divided into smaller parts, and these again into even smaller fragments, finally a level is reached of no longer divisible things. They called them *atomos*, which is the Greek name of atoms, the indivisible. The philosophers subscribed them with defined properties, namely to be:
- very small,
- and thus invisible,

- indivisible,
- hard,
- of different forms (however without color, taste or smell)
- moving spontaneously and continuously (in an empty space, i.e. *in vacuo* or in "ether").

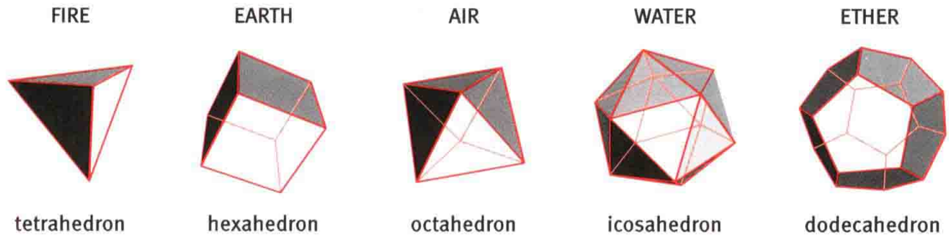

Figure 1.1: The five Platonic solids. Each is composed of a number of identical isosceles surfaces: tetrahedron (4 triangles), hexahedron (6 squares), octahedron (8 triangles), icosahedron (20 triangles), dodecahedron (12 pentagons).

To conceive of the ultimate building blocks[1] as having "different forms" included the elegant idea that the matter built of them finally reveals properties of the "atoms", which themselves remain invisible. Ultimately, the building blocks are not only the composites of our material world – they are responsible for its properties.

1.1.2 2000 years later: Experimental evidences

It took more than 22 centuries until this conceptual idea was proven experimentally. Chemists like Lavoisier (1743–1794), Proust (1755–1826) and Dalton (1766–1844) realized that individual chemical elements combine mass-wise to compounds according to some rules.

Conservation of mass (Lavoisier): The overall mass represented by all reaction partners remains constant. For a chemical reaction, the total mass is divided among all the species involved and, in the case of complete reaction, the mass of all reaction products is equal to the mass of the reactants. If hydrogen gas and oxygen gas undergo

1 It would become obvious only more than two thousand years later that this is not really true: It is more the number and the internal infrastructure of a well-defined, but small group of subatomic building blocks called "elementary particles" which define an "atom". These constructs, indeed define the physical and chemical properties of the atoms and chemical elements they create.

the oxyhydrogen gas reaction, e.g. 4 g of H_2 react with 16 g of O_2 (together making 36 g) to form 36 g of water. This experimental evidence is the law of conservation of mass (cf. Table 1.1).

Law of definite proportions (Proust): Species undergoing a chemical reaction combine not stochastically, but in characteristic ratios. Today, we know that this is according to the number of moles, which in turn represent the number of species. In the case where the two gases hydrogen and oxygen react to form water, hydrogen and oxygen combine in molar ratios of 2 : 1. According to their individual masses, this reflects a mass ratio of 1 : 8, whatever the different amounts of the two gases of hydrogen and oxygen were at the beginning of the chemical reaction. This experimental fact constitutes the law of definite proportions (cf. Table 1.1).

Table 1.1: The laws of conservation of mass and of definite proportions exemplified for the formation of water out of the two gases hydrogen and oxygen. The ratio between the two elements is always 1 : 8 if masses are counted, and 2 : 1 if moles are considered. Using the Avogadro number to convert moles into numbers of atoms, it is obvious that the overall number of atoms of the reactants (H_2 and O_2) is the same for the product (H_2O), and that the number of both hydrogen and oxygen atoms starting the reaction did not change, even if the reaction product is chemically a completely different species.

	$2\ H_2$	$+\ 1\ O_2$	→	2	H_2O
mass	$2 \times (2 \times 1\ g)$	$+\ 1 \times (2 \times 16\ g)$	=	2 x	$(2 \times 1 + 16)\ g = (2 : 16)\ g$
					mass ratio H : O = 1 : 8
		36 g	=	36 g	
mol	2×2 mol of H	1×2 mol of O		2 x	(2 mol of H + 1 mol of O)
					molar ratio H : O = 2 : 1
atoms	$4 \times 6.203 \cdot 10^{+23}$	$+\ 2 \times 6.203 \cdot 10^{+23}$	=	2 x	$(2 \times 6.203 \cdot 10^{+23} + 1 \times 6.203 \cdot 10^{+23})$
total		$6 \times 6.203 \cdot 10^{+23}$	=	$6 \times 6.203 \cdot 10^{+23}$	
H		$4 \times 6.203 \cdot 10^{+23}$	=	$4 \times 6.203 \cdot 10^{+23}$	
O		$2 \times 6.203 \cdot 10^{+23}$	=	$2 \times 6.203 \cdot 10^{+23}$	

These chemical observations allowed Dalton (1766–1844) to develop a "modern" theory on atoms. The fundamental postulates in 1808 were:
- chemical elements consist of extremely small particles, the atoms,
- all atoms of one specific chemical element are identical, while
- atoms of different elements are different,
- chemical reactions just reflect the combination or separation of atoms,
- within these combination or separation reactions, atoms do not disappear, i.e. are not destroyed or created,
- no atom of one chemical element is transformed into an atom of a different chemical element,

- a chemical compound is the combination of characteristic atoms of one (e.g. H_2), two (e.g. H_2O) or more chemical elements,
- a specific chemical compound contains atoms in a fixed, compound-specific mass ratio (cf. Table 1.2).

DALTON'S key point was the renaissance of the assumptions made by the Greek philosophers more than two millenniums ago. Chemical elements (that is, matter) are made of atoms, representing the ultimate small, not further divisible constituents of elements (Fig. 1.2).

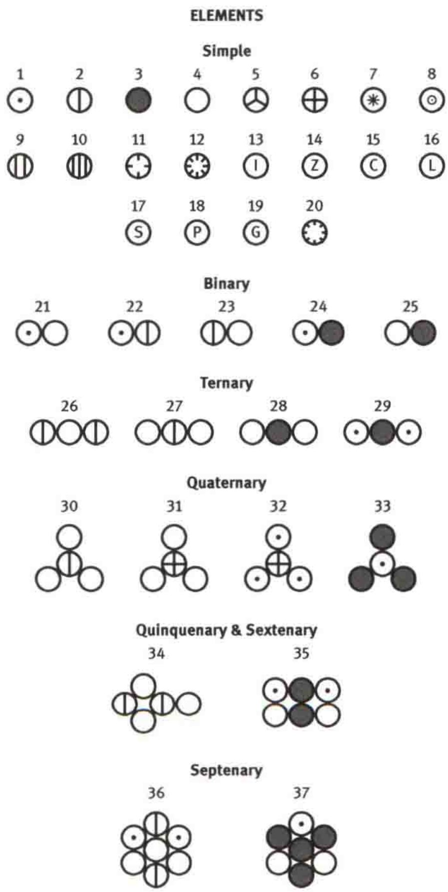

Figure 1.2: DALTON'S "New System of Chemical Philosophy" describing the elements with individual symbols and chemical compounds as individual elements interconnected in specific relationships (stoichiometry), without losing their identity.