

Jens-Volker Kratz, Karl Heinrich Lieser

Nuclear and Radiochemistry

Fundamentals and Applications

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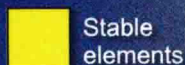
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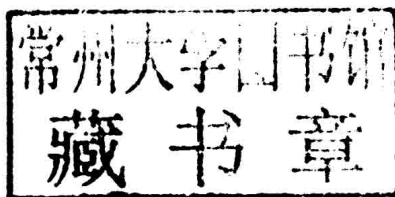


Jens-Volker Kratz and Karl Heinrich Lieser

Nuclear and Radiochemistry

Fundamentals and Applications

Third, revised edition



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Preface

This textbook aims at a complete and concise description of the present knowledge of nuclear and radiochemistry and applications in various fields of the natural sciences. It is based on teaching courses and research spanning several decades. The book is mainly addressed to advanced undergraduate students and to graduate students of chemistry. Students and scientists working in physics, geology, mineralogy, biology, medicine, and other fields will also find useful information about the principles and applications of nuclear and radiochemistry.

Traditionally, nuclear chemistry has been deeply tied to nuclear physics, cooperatively called nuclear science. At the same time, a wide field of applications of nuclear and radiochemistry in other sciences has developed. Therefore, it was considered important to bring together in one textbook a detailed presentation of the physical fundamentals as well as applied aspects of nuclear chemistry ranging from nuclear structure, nuclear masses, nuclear reactions, the production of radionuclides and labeled compounds, the chemistry of the radioelements, the study of radionuclides in the environment, all the way to the nuclear and radiochemistry needed in nuclear technology. Applications also include the use of radionuclides in analytical chemistry, in geo- and cosmochemistry, dating by nuclear methods, and the use of radionuclides in the life sciences and medicine.

For further reading, the relevant literature is listed abundantly at the end of each chapter. Generally, it is arranged in chronological order, beginning with the literature of historical relevance, followed by more recent work subdivided according to the subject matter into general and more specialized aspects.

After the passing of Professor Karl Heinrich Lieser, the younger author (JVK) was approached by the Lieser family and by the publisher and was motivated to prepare a generally updated third edition of this textbook. The concept and structure of the book remain largely unchanged; however, new developments and results have been incorporated, including the most recent references. These updates concern the physical properties of atomic nuclei, the nuclear force and nuclear structure, techniques in nuclear chemistry, nuclear reactions, statistical considerations in radioactivity measurements, the actinides and transactinides, radionuclide mass spectrometry, and modern methods of speciation of radionuclides in the environment. These have been

taken from teaching courses held at the Johannes Gutenberg University over the last 30 years.

It is my pleasure to thank Mrs. Petra Sach-Muth for help with the software “wiley-vch.dot” and Mr. Jürgen Hubrath for scanning and improving a large number of new figures.

Mainz, April 2012

Jens-Volker Kratz

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1

Fundamental Concepts

Nuclear and radiochemistry cover a wide spectrum of areas such as (i) studies of the chemical and physical properties of the heaviest human-made elements; (ii) studies of nuclear structure, nuclear reactions, and radioactive decay, (iii) studies of nuclear processes in the Universe, such as geochronology and cosmochemistry; and (iv) applications of radioactivity in a vast variety of fields such as radioanalysis, chemistry, life sciences, and industrial applications, and in the geo- and biosphere. Nuclear chemistry has ties to all traditional areas of chemistry. Nuclear chemists are involved in the preparation of radiopharmaceuticals for use in medicine. Radiometric techniques play an important role in analytical chemistry and are often used as references validating other analytical techniques. The study of the actinide and transactinide elements has traditionally involved nuclear chemists studying the limits of nuclear stability and the periodicity of the periodic table of the elements. The physical concepts at the heart of nuclear chemistry have their roots in nuclear physics. Thus nuclear physics and nuclear chemistry overlap and are cooperatively called nuclear science. However, there are distinctions between these related fields. Besides the close ties to chemistry mentioned above, nuclear chemists are studying nuclear problems in different ways than nuclear physicists. Nuclear physics tends to look into the fundamental interactions between subatomic particles and fundamental symmetries. Nuclear chemists have focused on more complex phenomena where statistical properties are important. Nuclear chemists are more involved in applications of nuclear phenomena. For example, the nuclear fuel cycle or the migration of radionuclides in the environment are so inherently chemical that they involve nuclear chemists almost exclusively. The other term, radiochemistry, refers to the chemical applications of radioactivity and of related phenomena. Radiochemists are nuclear chemists but not all nuclear chemists are radiochemists. There are many nuclear chemists who use purely instrumental, physical techniques for their research and thus their work is not radiochemistry.

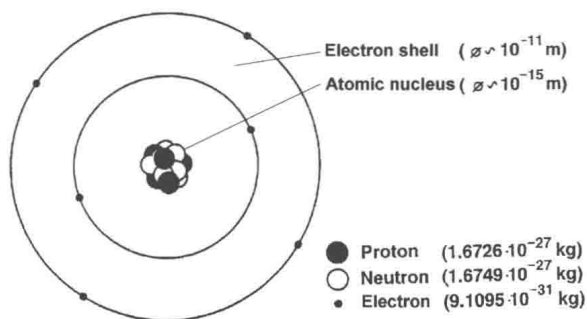


Figure 1.1 Schematic representation of the relative sizes of the atom and the nucleus.

1.1

The Atom

The atom is the smallest unit a chemical element can be divided into without losing its chemical properties. The radii of atoms are on the order of 10^{-10} m (Å). The atomic nucleus, see Figure 1.1, is a very small object with a radius on the order of $1\text{--}10 \cdot 10^{-15}$ m (femtometer, fm, called fermi) in the center of the atom and contains almost the entire mass of the atom. It contains Z protons, where Z is the atomic number of the element. Being the number of protons, Z is thus the number of positive charges in the nucleus. The nucleus also contains N neutrons, where N is the neutron number. Neutrons are uncharged particles with masses almost identical to the proton mass. Electrons surround the nucleus. Electrons are small negatively charged particles with a mass of $1/1836$ of the proton mass. The electrons are bound electrostatically to the positively charged nucleus. In a neutral atom, the number of electrons equals the number of protons in the nucleus. The chemistry of the element is controlled by Z . From quantum mechanics, we know that only certain discrete energies and angular momenta of the electrons are allowed. These quantized states are schematically depicted in Figure 1.1. Later, in Chapter 5, we will see also that nucleons occupy orbits with discrete energies and angular momenta. However, the sizes and energies of atomic and nuclear processes are very different, allowing us to consider them separately.

1.2

Atomic Processes

In the inelastic collision of two atoms, we can anticipate (i) excitation of one or both atoms involving a change in electron configuration; or (ii) ionization of one or both atoms, that is, removal of one or more electrons from the atom to form a positively charged ion. For this process to occur, an atomic electron must receive an energy exceeding its binding energy. This energy far exceeds the kinetic energies of gaseous atoms at room temperature. Thus, the atoms must have high

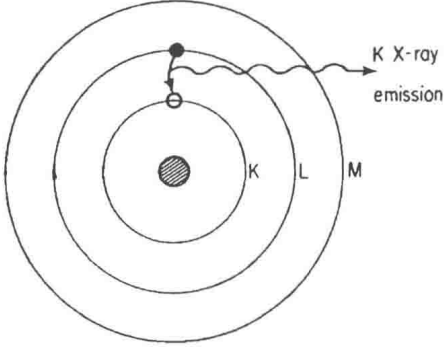


Figure 1.2 Scheme showing X-ray emission when a vacancy in an inner electron shell caused by nuclear decay is filled. An L-shell electron is shown filling a K-shell vacancy associated with K X-ray emission.

kinetic energies as a result of nuclear decay or acceleration to eject electrons from other atoms in atomic collisions. When an electron in an outer atomic electron shell drops down to fill a vacancy in an inner electron shell, electromagnetic radiation called X-rays is emitted. In Figure 1.2, an L-shell electron is shown filling a K-shell vacancy. In the transition, a characteristic K X-ray is emitted. The energy of the X-rays is equal to the difference in the binding energies of the electrons in the two shells, which depends on the atomic number of the element. Specifically, X-rays due to transitions from the L shell to the K shell are called K_{α} X-rays, while X-rays due to transitions from the M to K shells are termed K_{β} X-rays. Refining further, $K_{\alpha 1}$ and $K_{\alpha 2}$ designate transitions from different subshells of the L shell, that is, $2p_{3/2}$ (L_{III}) and $2p_{1/2}$ (L_{II}). X-rays for transitions from M to L are L_{α} X-rays. For each transition, the change in orbital angular momentum $\Delta \ell$ and total angular momentum Δj must be $\Delta \ell = \pm 1$ and $\Delta j = 0, \pm 1$.

For a hydrogen-like atom, the Bohr model predicts that the transition energy ΔE is

$$\Delta E = E_i - E_f = R_{\infty} h c Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (1.1)$$

where R_{∞} is the Rydberg constant, h the Planck constant, c the speed of light, and n the principal quantum number of the electron. The X-ray energy $E_x = -\Delta E$, after inserting the physical constants, is

$$E_x = 13.6 Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{eV} \quad (1.2)$$

For K_{α} X-rays from hydrogen-like atoms

$$E_x = 13.6 Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \text{eV} \quad (1.3)$$

and for L_{α} transitions

$$E_x = 13.6Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \text{eV} \quad (1.4)$$

In a realistic atom, Z must be replaced by $Z_{\text{effective}}$ to take care of the screening of the nuclear charge by other electrons. Henry Moseley showed that the frequencies, ν , of the K_{α} X-rays scale as

$$\nu^{1/2} = \text{const}(Z - 1) \quad (1.5)$$

and those of the L_{α} X-rays scale as

$$\nu^{1/2} = \text{const}(Z - 7.4) \quad (1.6)$$

Thus, Moseley showed that the X-ray energies, $h\nu$, depend on the square of an altered, effective atomic number due to screening. The relative intensities of different X-rays depend on the chemical state of the atom, its oxidation state, complexation with ligands, and generally on local electron density. The relative intensities are, therefore, useful in chemical speciation studies. As will be discussed in Chapter 6, radioactive decays can be accompanied by X-ray production and the latter may be used to identify the decaying nucleus.

1.3

Discovery of the Atomic Nucleus

Before the discovery of radioactivity, elements were considered as unchangeable substances. In 1897, J.J. Thomson discovered the electron and concluded that the atom must have a structure. As the mass of the electron is roughly 1/2000 of the mass of hydrogen, he concluded that most of the mass of the atom must be contained in the positively charged constituents. It was assumed that negative and positive charges are evenly distributed over the atomic volume.

In 1911, Ernest Rutherford studied the scattering of α particles in thin metal foils. He found that backscattering to $\theta > 90^\circ$ was more frequent than expected for multiple scattering from homogeneously charged atoms. This led Rutherford to postulate the existence of an atomic nucleus having mass and positive charges concentrated in a very small volume. The nucleus was supposed to be surrounded by electrons at the atomic diameter and the electrons do not contribute to the α -particle scattering. He postulated the following ansatz: the nuclear charge is Ze ; that of the α particle is $Z_{\alpha} = 2e$. The scattering force is the Coulomb force. The nucleus is at rest in the collision and the path of an α particle in the field of the nucleus is a hyperbola with the nucleus at the external focus. From these simplifying geometric properties and from the conservation of momentum and energy, Rutherford derived his famous scattering formula which relates the number $n(\theta)$ of α particles scattered into a unit area S at a distance r from the target foil F , see Figure 1.3, to the scattering angle θ