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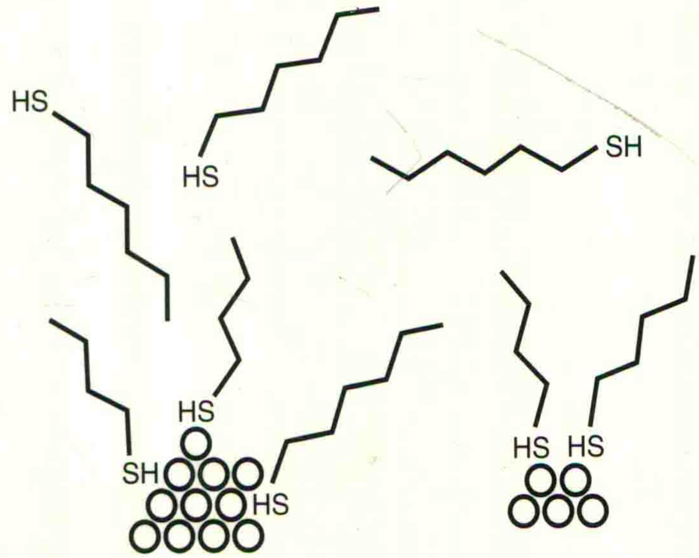
G.B. Sergeev



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Foreword

At the turn of the century when it seemed that everything in chemistry had already been discovered, understood, and just waiting to be applied to the benefit of mankind, a new interdisciplinary field—nanoscience—was born. This book is devoted to one of its directions, nanochemistry.

Chemists always knew and well understood the significance of atoms and molecules as the main 'blocks' in the huge foundation of chemistry. At the same time, the development of new precision, 'custom-made' instrumentation, such as high-resolution electron microscopy, probe scanning microscopy, highly selective mass spectrometry, in combination with special procedures for synthesizing samples provided insight into the behavior of particles of, e.g., metals that contain few, i.e., less than 100 atoms. Such particles measuring about 1 nm (10^{-9} m) exhibited unusual, hardly predictable chemical properties. It turned out that such nanoparticles or clusters display a high activity and provide an opportunity for carrying out reactions, which never occurred with macroscopic particles, in a wide temperature range. Nanochemistry concerns itself precisely with such fine particles.

One of the basic problems of nanochemistry is associated with finding out how the chemical properties depend on the size (or the number of atoms) of particles involved in the reaction. This problem can be solved most successfully in the gas phase at low temperatures or in inert matrices.

This monograph is written by Professor G.B. Sergeev of the Faculty of Chemistry, Moscow State University. He is a pioneer and the greatest contributor to the development in our country of such a unique direction as cryochemistry. His studies in theoretical and applied aspects of cryochemistry were acknowledged by awarding him the Lomonosov Prize.

In recent years, he and his pupils successfully elaborated a new direction in cryochemistry of metal atoms and nanoparticles. This monograph reflects the results of these studies together with a large body of literature information published in recent years. In fact, this is the first book on this science, which is rapidly developing all over the world, and it will allow the reader to acquaint with a new and interesting direction, named nanochemistry.

V.A. Kabanov, Member of the Russian Academy of Sciences

Dedication

In memory of Rimma, my beloved wife and friend.

Preface

This book is dedicated to a wonderful person, Rimma Vladimirovna Golovnya, Doctor of Chemistry. Professor R.V. Golovnya was a leading scientist in the field of gas chromatography and flavochemistry and worked fruitfully for many years in organic, analytical, and physical chemistry.

Being students, we were fortunate to enjoy lectures by academicians A.N. Nesmeyanov, P.A. Rehbinder, and V.I. Spitsin, professors of the Faculty of Chemistry at Moscow State University. The supervisor of my post-graduate training, academician N.N. Semenov, was the first among Russian chemists to win the Nobel Prize. It was he who suggested, immediately after I defended my Candidate of Chemistry Dissertation, that I should direct my efforts at studying the earlier unknown spontaneous reactions at low temperatures. Thus, the fast, virtually explosive reactions of halogenation, hydrohalogenation, and nitration of olefins in the vicinity of the boiling point of liquid nitrogen (77K) were discovered and studied; chain reactions that involved frozen-out radicals and combined the features of chain and thermal explosions were observed; the participation of molecular complexes in competitive cryochemical reactions that proceeded via molecular, ionic, and radical mechanisms was proved; and the spontaneous formation of free radicals in low-temperature reactions of halogens with olefins was established. Currently, cryochemistry represents an independent and constantly developing field.

In the early 1980s, we pioneered the studies of reactions in joint low-temperature condensates of vapors of magnesium and organic compounds. It is these studies that initiated the many year cycle of studies carried out at the Laboratory of Low Temperatures devoted to the synthesis, stabilization, and reactions of atoms and nanoparticles of different metals. At present, our group at the Faculty of Chemistry of Moscow State University is continuing the research in this direction. A number of our studies on the nanochemistry of metals were accomplished for the first time, and the dynamics of their development is described in detail in this monograph. A monograph written by the author and published in Russian in 2003 forms the basis of this book. The development of nanochemistry is so fast that the two years since the monograph's publication have allowed us to substantially increase the number of cited papers and to introduce a large number of new results obtained in recent years. Among the trends most actively developed at present, mention should be made of the great attention devoted to nanoparticles of various shapes and the impressive growth of publications in the fields of biology and medicine. In the past two years, the other directions of nanochemistry covered in the 2003 monograph were also actively developed, which allowed us to retain the original structure of the book and to add new material to many chapters. By definition, a monograph should reflect most comprehensively the subject chosen. However, this condition is difficult to fulfill for nanochemistry, because its development proceeds exponentially. In such cases, new monographs are of the greatest importance, as they make it possible to describe newly formulated ideas and take a new look at the known material.

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I am also grateful to my children and grandchildren, who kindly understood my preoccupation with the preparation of this book. I would like to thank all my colleagues for their attention to my concerns with this book and their valuable help. I am grateful to all those who took part in the preparation of this edition.

G.B. Sergeev

Introduction

Contemporary chemistry demonstrates a trend for a transition from carrying out experiments under 'ordinary' conditions (temperatures close to 300 K, normal concentrations, and atmospheric pressure) to conducting syntheses at superhigh energies and superlow temperatures, superhigh pressures and superhigh vacuum, superlow concentrations and with participation of supersmall or small-scale particles.

Particles of nanometer sizes began to attract the attention of scientists in different fields of science in the last 15–20 years. More active development in this direction dates back to the 1990s, when the first international conferences on nanomaterials were held and the first relevant scientific journals appeared. At present, the programs of many Russian and international congresses, conferences, and symposia include the subjects Nanoparticles, Nanoclusters, Nanocomposites, Nanotechnology, either as such or as constituents of the section subject.

This monograph is one of the first attempts to consider and systemize the studies in the field of nanochemistry. The term 'nanochemistry' appeared in the cited literature at the end of the 1990s. This direction is being explored very rapidly, and the situation is additionally complicated by its yet unsettled concepts and definitions. The experimental and theoretical material described in this monograph show that contemporary nanochemistry is a new, actively developing scientific direction. Like any other direction, nanochemistry has its own subject, objects for studying, and experimental methods, the analysis of which forms the major subject of this book.

A modern trend in the research of nanosized particles in physics, chemistry, and biology allows one to assert that in the 21st century both science and technology will deal with nanosized, angström objects ($2\,nm = 10^{-9}\,m$; $1\,Å = 10^{-10}\,m$). The interest of chemists in nanoparticles is explained as being due to several reasons. The chief reason is the fact that studying nanoparticles of various elements in the Periodic Table opens up new directions in chemistry that cannot be described in terms of already known relationships. Moreover, particles measuring less than 1 nm are of the greatest interest. This is explained by the fact that such formations of, e.g., metals contain approximately 10 atoms that form a superficial particle that has no volume and displays an enhanced chemical activity. At the same time, it is known that chemical properties and activity of a particle can be changed by the addition of just a single atom or molecule. The most fundamental problem of modern chemistry is to reveal the peculiarities of the effect of the particle size (or the number of atoms) on its physicochemical properties and reactivity.

Nowadays, the physicochemical properties and reactions of small particles in the gas phase and, recently, in solid and liquid phases are often described by the number of atoms or molecules rather than by their sizes in nanometers. Of certain value can be the scale of atomic/molecular diameters, where the particles comprising 1–100 atomic/molecular diameters are most interesting. In such a range of sizes, the different relationships between the chemical properties and the number of atoms in a particle are observed most frequently.

The experimental material obtained to date makes it possible to define nanochemistry as a field that studies synthesis, properties, and reactivity of particles and assemblies they form, which measure less than 10 nm at least in one direction. Apparently, the value 10 nm is arbitrary; however, its introduction plays a certain role, stressing the subject of nanochemistry. Moreover, a size of 10 nm and the aforementioned definition show that nanochemistry deals with one-, two-, and three-dimensional objects such as films, wires, and tubes. On the other hand, this rules out the assignment of particles larger than 10 nm to nanochemistry. Particles with sizes approaching 100nm would be more correctly classified as ultradispersed, and materials on their basis as microscopic.

Contemporary nanochemistry accumulates experimental material and develops its theoretical interpretation. Unusual chemical properties of particles consisting of a small number of atoms, i.e., several tens of atoms, require a serious modification of concepts developed for systems that involve thousands and millions of atoms. Studies in the field of nanochemistry open up possibilities for the formation of new paradigms of synthesizing substances with remarkable, earlier unknown properties.

In this monograph, attention is focused on synthesis and chemical reactions of atoms, clusters, and nanoparticles based on metals of different groups in the Periodic Table. A separate chapter is devoted to nanoparticles based on carbon. The formation of metal cores, clusters, and nanoparticles begins as a rule with atoms. To correctly understand such processes, it is vital to get to the bottom of chemical properties of atoms; thus, the participation of certain reactions are reflected upon in this book. Methods for synthesizing, stabilizing, and studying nanoparticles are discussed relatively briefly. Multicomponent systems, hybrid and film materials with various chemical properties are analyzed. Great attention is devoted to size effects in chemistry, which are associated with the *qualitative* changes in physicochemical properties and reactivity depending on the *quantity* of species in a particle and proceed in a range smaller than 10 nm. Semiempiric and *ab initio* quantum-chemical approaches to theoretical description of nanoparticle properties are briefly outlined. A separate chapter is devoted to studies on cryochemistry of metal atoms and nanoparticles. This field of nanochemistry is actively explored by the author of this monograph and his pupils and colleagues in cooperation with Russian and foreign scientists. The sections providing an outlook on various applications of nanoparticles and relevant materials in science and technology are collected in a special chapter. Problems and prospects in the development of nanochemistry and nanotechnology as well as the use of nanoparticles in biology and medicine are discussed.

The monograph can be considered, on the one hand, as an introduction to a new field of chemistry and, on the other, as a sort of a guidebook to the extensive literature devoted to the chemistry of nanoparticles. For the most part, it comprises the studies published in the past 3–4 years. In addition to original literature, the materials of lecture courses held by the author at the Faculties of Chemistry and Material Sciences of the Moscow State University were used. This fact introduces certain elements of a study-book into the material of several sections.

First of all, this book should be interesting for those who wish to get acquainted with this new scientific field, in which the concepts of physics, chemistry, and material science are closely interlinked. The book will also be helpful for those scientists and pedagogues who develop different concrete aspects of nanoscience as well as for students and post-graduate students who want to direct their efforts to studying this new and challenging field.

Contents

– 1 –

Survey of the Problem and Certain Definitions

Nowadays, we are witnessing the development and advancement of a new interdisciplinary scientific field—nanoscience. Despite its name, it cannot be associated solely with miniaturization of the studied objects. In fact, nanoscience comprises closely interrelated concepts of chemistry, physics, and biology, which are aimed at the development of new fundamental knowledge. As was shown by numerous examples in physics, chemistry, and biology, a transition from macrosizes to those of 1–10 nm gives rise to qualitative changes in physicochemical properties of individual compounds and systems.

The historical aspect of the formation and development of independent fundamental directions of nanoscience and the prospects of their application in different branches of nanotechnology were discussed in detail in numerous reviews.[1–4] Numerous books and articles by Russian scientists who had a great influence on the progress in studying small-scale particles and materials can be found in Ref. 3. Their contribution was acknowledged to a certain extent by the 2000 Nobel Prize, which was awarded to Zh.I. Alferov for his achievements in the field of semiconducting heterostructures.

In the past 10–15 years, the progress in nanoscience was largely associated with the elaboration of new methods for synthesizing, studying, and modifying nanoparticles and nanostructures. The extensive and fundamental development of these problems was determined by nanochemistry. Nanochemistry, in turn, has two important aspects. One of these is associated with gaining insight into peculiarities of chemical properties and the reactivity of particles comprising a small number of atoms, which lays new foundations of this science. Another aspect, connected to nanotechnology, consists of the application of nanochemistry to the synthesis, modification, and stabilization of individual nanoparticles and also for their directed self-assembling to give more complex nanostructures. Moreover, the possibility of changing the properties of synthesized structures by regulating the sizes and shapes of original nanoparticles deserves attention.

The advances in recent studies along the directions mentioned are reflected in several reviews and books.[5–13] A special issue of the journal *Vestnik Moskovskogo Universiteta* was devoted to the problems of nanochemistry.[14] The dependence of physicochemical properties on the particle size was discussed based on optical spectra,[15] magnetic properties,[16,17] thermodynamics,[18] electrochemistry,[19] conductivity, and electron transport.[20,21] Different equations describing physical properties as a function of the particle size were derived within the framework of the droplet model.[22] A special issue of *Journal of Nanoparticle Research* is devoted to the works of Russian investigators in the field of nanoscience.[23] Many aspects of synthesis, physicochemical properties and self-assembly have been reviewed.[24]

In nanochemistry, which is in a stage of rapid development, questions associated with definitions and terms still arise. The exact difference between such terms as "cluster," "nanoparticle," and "quantum dot" has not yet been formulated in the literature. The term "cluster" is largely used for particles that include small numbers of atoms, while the term "nanoparticle" is applied for larger atomic aggregates, usually when describing the properties of metals and carbon. As a rule, the term "quantum dot" concerns semiconductor particles and islets, the properties of which depend on quantum limitations on charge carriers or excitons. In this book, no special significance will be attached to definitions, and the terms "cluster" and "nanoparticle" will be considered as interchangeable.

Table 1.1 shows some classifications of nanoparticles, which were proposed by different authors based on the diameter of a particle expressed in nanometers and the number of atoms in a particle. These classifications also take into account the ratio of surface atoms to those in the bulk. A definition given by Kreibig[25] is similar to that proposed by Gubin.[26] It should be mentioned that a field of chemistry distinguished by Klabunde[12] pertains in fact to particles measuring less than 1 nm.

Nanoparticles and metal clusters represent an important state of condensed matter. Such systems display many peculiarities and physical and chemical properties that were never observed earlier. Nanoparticles may be considered as intermediate formations, which are limited by individual atoms on the one hand, and the solid phase on the other. Such particles exhibit the size dependence and a wide spectrum of properties. Thus, nanoparticles can be defined as entities measuring from 1 to 10 nm and built of atoms of one or several elements. Presumably, they represent closely packed particles of random shapes with a sort of structural organization. One of the directions of nanoscience deals with various properties of individual nanoparticles. Another direction is devoted to studying the arrangement of atoms within a structure formed by nanoparticles. Moreover, the relative stability of individual parts in this nanostructure can be determined by variations in kinetic and thermodynamic factors. Thus, nanosystems are characterized by the presence of various fluctuations.

Natural and technological nanoobjects represent, as a rule, multicomponent systems. Here again, one is up against a large number of different terms, such as "nanocrystal," "nanophase," "nanosystem," "nanostructure," "nanocomposites," etc., which designate formations built of individual, separate nanoparticles. For instance, nanostructure can be defined as an aggregate of nanoparticles of definite sizes, which is characterized by the presence of functional bonds. In the reactions with other chemical substances, such limited-volume systems can be considered as a sort of nanoreactors. Nanocomposites represent systems where nanoparticles are packed together to form a macroscopic sample, in which interactions between particles become strong, masking the properties of individual particles. For every type of interaction, it is important to know how the properties of a sample change with its size. Moreover, it should be mentioned that with a decrease in the particle size, the concept of phase becomes less clear: it is difficult to find boundaries between homogeneous and heterogeneous phases, and between amorphous and crystalline states. At present, the common concepts of chemistry, which define the relationships such as composition–properties, structure–function, are supplemented by the concepts of size and

Table 1.1

Classification of particles by their sizes

(a)

U. Kreibig [25]			
Domain I Molecular clusters	Domain II Solid-state clusters	Domain III Microcrystals	Domain IV Bulk particles
$N \le 10$ Indistinguishable surface and volume	$10^2 \le N \le 10^3$ Surface/volume ratio ≈ 1	$10^3 \le N \le 10^4$ Surface/volume ratio <1	$N > 10^5$ Surface/volume ratio <1

(b)

K. Klabunde [12]											
Chemistry					Nanoparticles				Solid-state physics		
Atom	$N = 10$		$N = 10^2$		$N = 10^3$		$N = 10^4$		$N = 10^6$	Bulk matter	
Diameter (nm)		1		2		3	5	7	10		>100

(c)

N. Takeo (*Disperse Systems*, Wiley-VCH, p.315, 1999.)		
Superfine clusters	Fine clusters	Coarse clusters
$2 < N \le 20$ $2R \le 1.1$ nm Indistinguishable surface and internal volumes	$20 < N \le 500$ 1.1 nm $\le 2R \le$ 3.3 nm $0.9 \ge N_s/N_v \ge 0.5$	$500 < N \le 10^7$ 3.3 nm $\le 2R \le$ 100 nm $0.5 \ge N_s/N_v$

(d)

G.B. Sergeev, V.E. Bochenkov (Physical Chemistry of Ultradispersed Systems: Conference Proceedings, Moscow, 2003, pp.24–29.)										
Chemistry of atoms	Nanochemistry Number of atoms in particle									Chemistry of solid state
Single atoms	10		10^2		10^3		10^4		10^6	Bulk
Diameter (nm)		1		2		3	5	7	10	>100

self-organization, giving rise to new effects and mechanisms. Nonetheless, despite all achievements of nanochemistry, we still cannot give a general answer to the question how the size of particles of, e.g., a metal, is related to their properties.

Metallic nanoparticles measuring less than 10 nm represent systems with excessive energy and a high chemical activity. Particles of about 1 nm need virtually no activation energy to enter into either aggregation processes, which result in the formation of metal nanoparticles, or reactions with other chemical compounds to give substances with new properties. The stored energy of such particles is determined first of all by uncompensated bonds of surface and near-surface atoms. This can give rise to unusual surface phenomena and reactions.

The formation of nanoparticles from atoms involves two processes, namely, the formation of metal nuclei of different sizes and the interactions between the formed particles, which generate the formation of assemblies that possess a nanostructure.

Virtually all methods of nanosynthesis produce nanoparticles in nonequilibrium metastable states. On the one hand, this factor complicates their investigation and application in nanotechnologies aimed at the development of stable devices. On the other, nonequilibrium systems allow carrying out new unusual chemical reactions, which are difficult to predict.

Elucidation of the relationship between the size and chemical reactivity of a particle is among the most important problems of nanochemistry. For nanoparticles, two types of size effects are distinguished.[27] One of these is their intrinsic or internal effect, which is associated with specific changes in superficial, bulk, and chemical properties of a particle. The other, external effect, represents a size-dependent response to external factors unrelated to the internal effect.

Specific size effects manifest themselves to a great extent for smaller particles and are most likely in nanochemistry, where irregular size–properties dependencies prevail. The dependence of activity on the size of particles taking part in a reaction can be associated with the changes in the particle properties in the course of its interaction with an adsorbed reagent,[28] correlations between geometrical and electron-shell structures,[29] and symmetry of boundary orbitals of a metal particle with respect to adsorbed-molecule orbitals.[30]

As mentioned above, nanochemistry studies the synthesis and chemical properties of particles and formations with sizes below 10 nm along one direction at least. Moreover, most interesting transformations are associated with the region of ca. 1 nm. Elucidation of mechanisms that govern the activity of particles with sizes of 1 nm and smaller is among the major problems of modern nanochemistry, despite the fact that the number of particles is a more fundamental quantity as compared with their size.

The dependence of chemical activity on the size of reacting particles is explained by the fact that properties of individual atoms of elements as well as of clusters and nanoparticles formed from atoms differ from the properties of corresponding macroparticles. To understand and roughly analyze the size-dependent chemical properties, we can compare the reactivities of compact substances, nanoparticles, and clusters of species.[31] The demarcation lines between sizes of such formations vary from element to element and should be specified for each case.

In nanochemistry, the interaction of every particle with the environment has its own specifics. When studying individual properties of such a particle, attention should be focused on qualitative changes in particle properties as a function of its size. Moreover, the properties of isolated nanoparticles are characterized by a wide statistical scatter, which varies in time and requires special studies.

The internal size effect in chemistry can be caused by the changes in the particle structure and the surface-induced increase in the electron localization. Surface properties affect the stabilization of particles and their reactivity. For small numbers of reagent atoms adsorbed on the surface, a chemical reaction cannot be considered as in infinite volume, due to the commensurable surfaces of a nanoparticle and a reactant.

Reaction kinetics in small-scale systems with limited geometry differs from classical kinetics, because the latter ignores fluctuations in concentrations of reacting particles. Formations containing small numbers of interacting molecules are characterized by relatively wide fluctuations in the number of reactants. This factor gives rise to a time lag between the changes in reactant concentration on the surfaces of different-size nanoparticles and, as a consequence, to their different reactivity. Kinetics of such systems is described based on a stochastic approach,[32] which takes into account statistical fluctuations in the number of reacting particles. The Monte-Carlo technique was also used for describing the kinetics of processes that occur on the surface of nanoparticles.[33]

In nanoparticles, a considerable number of atoms pertain to the surface, and their ratio increases with a decrease in the particle size. Correspondingly, the contribution of surface atoms to the system's energy increases. This has certain thermodynamic consequences, for example, a size dependence of the melting point T_m of nanoparticles. The size, which determines the reactivity of particles, also gives rise to effects such as variations in the temperature of polymorphous transitions, a solubility increase, and a shift of chemical equilibrium.

Experiments and theoretical studies on thermodynamics of small particles testify that the particle size is an active variable, which, together with other thermodynamic variables, determines the state of the system and its reactivity. The particle size can be considered as an equivalent of the temperature. This means that nanoscale particles can enter into reactions untypical of bulk substances. Moreover, it was found that variations in the size of metal nanocrystals control the metal–nonmetal transition.[34] This phenomenon is observed for particles with diameters not exceeding 1–2 nm and can also affect the reactivity of the system. The activity of particles also depends on interatomic distances. Theoretical estimates by the example of gold particles have shown that average interatomic distances increase with a decrease in the particle size.[35]

As a rule, nanoparticles, free of interactions with the environment, can exist as separate particles only in vacuum, due to their high activity. However, using the example of silver particles with different sizes, it was shown that optical properties are identical in vacuum and upon condensation in an argon medium at low temperatures.[36] Silver particles were obtained by mild deposition in solid argon. Spectra of clusters comprising 10 to 20 silver atoms resembled those of particles isolated in the gas phase by means of mass spectrometry. Based on these results, it was concluded that deposition processes have no effect on the shape and geometry of clusters. Thus, the optical properties and reactivity of metal nanoparticles in the gas phase and inert matrices are quite comparable.

A different situation is observed for nanoparticles obtained in the liquid phase or on solid surfaces. In the liquid phase, the formation of a metal nucleus of a particle from atoms is accompanied by interaction of particles with the environment. The interplay of these two processes depends on many factors, most important of which are the temperature and the reagent ratio in addition to physicochemical properties of metal atoms and the reactivity and stabilizing properties of ligands of the medium. The interaction of atoms and metal clusters with a solid surface is an intricate phenomenon. The process depends on the surface properties (smooth facet of single crystals and rough and developed surfaces of various adsorbents) and the energy of particles to be deposited.

As mentioned above, the main problem of nanochemistry is to elucidate the relationship between the size and chemical activity of particles. Based on experimental data available, we can formulate the following definition: size effects in chemistry are the phenomena that manifest themselves in *qualitative* changes in chemical properties and reactivity and depend on the number of atoms or molecules in a particle.[37]

It is difficult to regulate the size of metal nanoparticles that is often poorly reproducible, being determined by their preparation method. The mentioned factors limit the number of publications containing an analysis of the effect of particle size on its reactivity. In recent publications, such reactions were most actively studied in the gas phase, and experimental studies were supplemented by a theoretical analysis of the results obtained.

Chemical and physical properties of metal nanoparticles formed of atoms were observed to change periodically depending on the number of atoms in a particle, its shape, and the type of its organization. In this connection, attempts were undertaken to tabulate the electronic and geometrical properties of clusters and metal nanoparticles by analogy with the Mendeleev Periodic Table. As was shown by the example of sodium atoms, Na_3, Na_9, and Na_{19} particles are univalent, while halogen-like clusters Na_7 and Na_{17} exhibit enhanced activity. The lowest activity is typical of particles with closed electron shells, namely, Na_2, Na_8, Na_{18}, and Na_{20}.[38] This analogy, which was demonstrated for small clusters with properties determined by their electronic structure, makes it possible to expect the appearance of new chemical phenomena in reactions with such substances.

For sodium clusters containing several thousand atoms, periodic changes in the stability of particles were also revealed. For Na particles containing more than 1500 atoms, the closed-shell geometry prevails, which resembles that of inert gases.

It was noted[38] that the size of particles containing tens of thousand atoms can affect their activity in a different manner. Sometimes, the key role is played by electronic structures of each cluster; otherwise, the geometrical structure of the electronic shell of the whole particle has a stronger effect on the reactivity. In real particles, their electronic and geometrical structures are interrelated and it is not always possible to separate their effects.

The problem of elucidating the dependence of chemical properties on the size of particles involved in a reaction is closely linked with the problem of revealing the mechanisms of formation of nanoscale solid phases during electrocrystallization. Interactions of atoms in the gas and liquid phases or upon their collision with a surface first of all give rise to small clusters, which can later grow to nanocrystals. In the liquid phase, such nucleation is accompanied by crystallization and solid-phase formation. Peculiarities of the formation of nanoscale phases during fast crystallization were considered on qualitative and quantitative levels.[39,40] Nanochemistry of metal particles formed by small numbers of atoms demonstrates no pronounced boundaries between phases and the questions of how many atoms of one or other element are necessary for spontaneous formation of a crystal nucleus that can initiate the formation of a nanostructure have not yet found the answer.

In nanochemistry, when studying the effect of the particle size on its properties, the most important factors are the surface on which the particle is located and the nature of the stabilizing ligand. One of the approaches to solving this problem is to find the symmetry energy of the highest occupied molecular orbital and/or the lowest unoccupied molecular orbital as a function of the particle size. Yet another approach is based on finding such a shape of nanoparticles that would allow the optimal conditions for the reactions to be reached.

To date, nanochemistry of some elements of the Periodic Table was studied in sufficient detail, while other elements were studied incompletely.

From our viewpoint, in the next 10–15 years, the role of nanochemistry in the development of nanotechnology will increase; this is why in the following chapters we will discuss in detail the synthesis, chemical properties, and reactivity of atoms, clusters, and nanoparticles of different elements in the Periodic Table.