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Chemical research at the Saint-Petersburg State University



This issue of the Journal is compiled from reviews written by researchers of the Department of Chemistry and the Research Institute for Chemistry of the Saint-Petersburg State University.

The Department of Chemistry, which celebrated its 75th anniversary in 2004, descends from the Division of Chemistry of the Physico-Mathematical Department of the Imperial Saint-Petersburg University. Teaching chemistry at the University began in the 1830s, and in 1868 the Division of Chemistry, which had expanded considerably by that time, was split into three sectors, *viz*., inorganic, organic and analytical chemistry, headed by D I Mendeleev, A M Butlerov and N A Menshutkin, respectively. Academicians D P Konovalov, V E Tishchenko, A E Favorsky, S V Lebedev, V G Khlopin, B P Nikolsky, I I Chernyaev, A A Baikov, the Corresponding Members of the RAS M S Vrevsky, I I Zhukov, Professors L A Chugaev, S A Shchukarev, R L Müller, Ya V Durdin, A V Storonkin and other outstanding representatives of Russian science had been working at the Institute at different times.

In 1934, the Educational-and-Research Centre for Chemistry (RECC) was established on the base of the Department of Chemistry and the newly founded Research Institute for Chemistry. In 2003, the Institute for Laser Research acceded to them.

To date, the staff of the Department and the Institutes comprises Academicians A I Rusanov and M M Shults, Corresponding Members of the RAS N A Smirnova and V B Aleskovsky, 70 professors and Doctors of Science and about 300 Ph.Ds. The results of investigations carried out in the past decade and documented in more than 2400 articles and reviews in Russian and foreign periodicals, 38 monographs, 84 manuals and 33 transactions have been published and 13 patents have been granted; over 200 grants from RFBR, RFBR-DFG, RFBR-INTAS, CRDF, DAAD, INTAS, the Volkswagen Foundation, NWO, INCO-COPERNICUS and various research programmes including the NATO Science Programme, Universities of Russia and programmes of the Ministry for Education and Science and the Ministry of Defence of the Russian Federation have been obtained.

The Department of Chemistry is collaborating successfully with many classical Russian universities, institutes of the RAS, academies of sciences, research establishments and manufacturing companies in the USA, Canada, Japan, China, Korea, SAR and the majority of European countries and takes an active part in organising various conferences, symposia and seminars.

The research activities at the Department are inseparably joined with educational work. The Department is carrying out large-scale training of specialists in virtually all chemical specialities. The Department admits annually 150 students from various regions of Russia. Many of its graduates take a post-graduate course to get a Ph.D. degree and some of these continue to work for a D.Sci. degree.

At present, the Department of Chemistry and its two Institutes comprise 13 divisions and 17 sectors on quantum chemistry, colloid chemistry, physical chemistry, chemical thermodynamics and kinetics, electrochemistry, general and inorganic chemistry, analytical chemistry, organic chemistry, physical organic chemistry, polymer chemistry, chemistry of natural compounds, radiochemistry, chemistry of solids, semiconductors and laser research.

The main areas of research at the ***Division and Sector of Quantum Chemistry*** include development of theoretical-group methods for the study of electronic and vibrational structures of complex molecules and crystals; studies into the nature of chemical bonds in crystalline solids (transition metal oxides, high-temperature superconductors, fullerenes); studies of vibrational characteristics of complex crystals; development of methods for calculation of electronic structures, electronic spectra, valence structures and magnetic characteristics of complex transition metal derivatives; further development of the theory of atomic structures with special reference to relativistic, quantum-electrodynamic and environmental phenomena; non-empirical calculations of potential energy surfaces of ground and excited states of metastable and excimeric cations; development of the theory on atomic valence in molecules, radicals and crystals; quantum chemistry of organic compounds.

The Division and Sector of Colloid Chemistry are among the world leaders in many fields, *e.g.*, electrokinetic phenomena, thermodynamics of surface effects, physicochemical hydrodynamics of capillary systems, micelle formation and surface separation of compounds. The discoveries in these fields are related to the behaviour of surface layers, mechanochemistry, wetting and nucleation. Fundamental results have been obtained in the theory of micelle formation, the theory of wetting of rough surfaces taking account of linear phenomena, the theory of foams, capillary waves and currents as well as computer simulation of minor systems including clusters of polar compounds. Considerable progress has been achieved in the study of structural, adsorption, electrokinetic and filtration characteristics of real and model disperse systems and membranes of various chemical origin including porous glasses; also in the study of surface tension, surface electric charge and surface potential, surface conductivity and surface separation processes. The theory of the equation of state has been developed in recent years. This line of research has been described in the review by Academician A I Rusanov 'Novel approach to the equation of state for fluid systems, based on the concept of the exclusion factor'.

Studies on ion-exchange, ionometry and redoxometry are among the main areas of research at ***the Division and Sector of Physical Chemistry***. Other trends include thermodynamics and molecular-statistical simulation of fluid systems [study of quantitative relationships between molecular characteristics of compounds and macroscopic properties of their solutions (fluid phases)]; development of novel versions of quasi-chemical models of solutions; development of a *p*-type quasi-chemical model of the fluid phase in a group variant; experimental studies and simulation of phase equilibria of fluid systems using the Monte Carlo method; thermodynamics of liquid-crystalline systems, *etc*. The review by the Corresponding Member of the RAS N A Smirnova 'Phase behaviour and self-assembly patterns of surfactant mixtures in solutions' is an overview of the state-of-the-art in solutions of surfactant mixtures.

The Division and Sector of Chemical Thermodynamics and Kinetics are carrying out research on heterogeneous equilibria in multicomponent systems, thermodynamics of reaction-mass-exchange processes, thermodynamics and kinetics of processes in high-temperature oxide systems, phase diagrams of water–salt systems, *etc*. Other trends include simulation of the thermodynamic behaviour of electrolyte solutions at high concentrations; thermodynamics of membrane processes; kinetics of liquid-phase reactions in strongly non-ideal concentrated media; complex intermolecular interactions (bifurcated hydrogen bonds, general acid–base catalysis, *etc*.); multimolecular intermediate reactive associates; structure and thermodynamics of aqueous solutions of organic compounds and their reactivities in aqueous media.

Studies on equilibria and kinetics of electrode processes in electrolyte solutions of variable compositions are traditional subjects of investigation at ***the Division and Sector of Electrochemistry***. These include analysis of the effects of double electrical layer structures on the rates of electrode reactions and processes complicated by chemical reactions in bulk. An entirely new trend, *viz*., electrochemistry of modified electrodes coated with conducting polymeric inorganic or organic films with mixed ion-electronic conductivities, has been developing successfully in the past decade.

Studies on coordination and cluster compounds and molecular complexes occupy a prominent place in the research carried out at ***the Division and Sector of General and Inorganic Chemistry***. A general theory of the electronic structures of transition-metal clusters with weak- and strong-field ligands has been developed together with the methodology for structural-and-dynamic simulation of intramolecular electron transfer in polynuclear organometallic transport chains. The most important in principle achievements include the discovery of novel classes of conversions of unsaturated organic ligands on polynuclear coordinating centres; development of a model of vibrational quantum tunnelling of electrons and the theory of a redoxonic mechanism for solid-phase vibrational redox reactions; rationalisation of high-temperature superconductivity, giant magnetoresistivity, electron-ionic conductivity of oxides with heterovalent atoms, *etc*. Studies on the structures and properties of aqueous solutions of salts, thermodynamics and kinetics of gas-phase reactions, nature of the donor–acceptor bonds in molecular complexes, *etc*., are under way.

The studies at ***the Department and Sector of Analytical Chemistry*** are developing along several lines, *viz*., separation methods and hybrid methods of analysis, spectroscopic methods, studies of reactivities of complexes, *etc*. The main achievements include the development of novel chromatographic methods of analysis, such as gas–liquid and gas–liquid-absorption chromatography, chromatomembrane flow techniques for continuous separation of substances, detection methods based on Zeeman modulation polarisation spectroscopy, Mössbauer and X-ray low-angle dispersion spectroscopy and discovery of new ligand reactions in complexes. Researchers at the Division are actively developing luminescent and electrochemical methods along with methods for flow-injection, vapour-phase and capillary-electrophoretic analysis including those based on the use of microchips. Each of these trends has found practical application: on-line ecological monitoring of waters has been substantiated methodologically and novel technologies for flow-injection, spectral analysis and oxygenation of blood, deoxygenation of water and homogeneous catalysis have been developed. The review by A L Moskvin and L N Moskvin 'Water and aqueous environments: on-line chemical analysis, problems and solutions' is devoted to flow-through methods of analysis, while the review by N A Bokach and V Yu Kukushkin 'Addition of HO-nucleophiles to free and coordinated nitriles' deals with novel reactions of ligands within complexes.

The main attention among other research trends developed at ***the Division and Sector of Organic Chemistry*** is given to the chemistry of unsaturated compounds, strained carbo- and heterocycles, study of rearrangements (including tautomeric conversions), reactions involving carbenes and reactivities of organic compounds. Novel five- and seven-membered oxygen- and nitrogen-containing heterocyclic compounds with potential biological activities have been prepared and novel approaches to the synthesis of unnatural or hardly accessible natural amino acids have been developed. The review by A F Khlebnikov, M S Novikov and R R Kostikov 'Iminium ylides from carbenes and carbenoids: generation and synthetic applications' is devoted to various reactions of carbenes.

The main areas of research at ***the Division and Sector of Physical Organic Chemistry*** are studies of the mechanisms of various hetero- and homolytic reactions. Considerable progress has been achieved in the theoretical and experimental design of principles and models for identification of mechanisms of chemical reactions and control over their selectivity; in-depth studies of tautomeric conversions in the synthesis of novel anion-selective ligands, *etc*. Such areas as metal-complex catalysis, directed synthesis of heterocyclic systems and especially the novel promising trend, chemistry of ecotoxicants, *etc*., are also developing successfully.

The activities at ***the Division and Sector of Polymer Chemistry*** are aimed at the synthesis and investigation of novel types of polymers with miscellaneous functions (*e.g.*, biodegradable polymers, dendritic macromolecules, *etc*.). The principles and methods for the preparation of dendritic polymers based on natural trifunctional amino acids that are promising for chromatography and the study of transport processes in biosystems have been developed. The self-assembly of dendritic macromolecules based on electrostatic interactions of a polyelectrolyte core with dendrons oppositely charged at the focal point has been carried out for the first time. A new method for the formation of porous polymeric materials for tissue engineering has been developed on the basis of biodegradable polymers.

Methods for the preparation of practically important peptides, *e.g.*, human insulin, bradykinin, vasopressin, oxytocin and its analogues, luliberin and its analogues, δ-sleep peptide, angiotensins I and II, somnogenic peptides, neurotensin, cholecystokinin, bombesin and its analogues, *etc.*, have been developed at ***the Division and Sector of Chemistry of Natural Compounds***. Schemes for the total synthesis of steroid estrogen analogues have been developed and their crystal and solution structures have been investigated. Novel compounds manifesting selective biological activities (predominantly, antisclerotic, osteoprotective or immunosuppressive) together with low hormonal activities have been prepared; the biological properties of many natural compounds have been investigated.

The Division and Sector of Radiochemistry are carrying out research in various fields of the physicochemistry of radionuclides. These investigations include studies of the nuclear prehistory and its effect on the nature of radiation-induced damage of metals; structures and migration of admixture 'hot' atoms (admixture radiation defects) formed in metals and alloys upon nuclear fission and transmutation induced by charged species, neutrons or upon radioactive decay; diffusion-thermal methods for isolation of radionuclides in the absence of substrates. Tracer methods were used to study the properties of membranes of chemical sensors [diffusion, electroconductivity, ion exchange (solution/solids) and novel chemical sensors for detecting heavy metals, *etc.*] and sensory systems of the 'electronic language' type have been developed.

Research at ***the Division and Sector of Chemistry of Solids*** is being carried out in such fields as ionics of solids, chemistry of highly organised substances, chemistry of surfaces and surface compounds, chemistry of nanostructures and nanostructurised materials, UV-Vis and IR spectroscopy of surfaces and nanostructures, precision synthesis of highly organised solids and nanostructurised materials, *etc.* A new line of research, *viz.*, chemistry of highly organised compounds, has appeared. Methods for the synthesis of solids and materials based on the 'backbone hypothesis' have been devised. The molecular layering method was used as a basis for the development of sorbents, catalysts, luminophores, dispersely reinforced composite materials, thin-film structures for electronic engineering, *etc.*

Medium-order studies of various processes occurring in glasses and glass-forming melts, 'semiconductor – metal' transitions and of the nature of the superionic state are being carried out at ***the Sectors for Semiconductors and Laser Investigations***. Highly effective materials for IR optical amplifiers, which represent nanostructurised chalcogenide glass films doped with rare-earth ions, have been prepared for the first time by UV-laser sputtering in the framework of a novel direction of investigations, *viz.*, laser materials science. Special attention is given to the interaction of laser irradiation with a material and concomitant chemical reactions. The effect of fundamental photo-induced changes in the optical width of the forbidden gap and the refraction indices of chalcogenide films prepared by laser sputtering have been determined.

This issue includes only some of the reviews prepared by researchers of the Department of Chemistry of SPbSU. The reviews summarising the results of investigations in other areas of research will be published in the next issues of the Journal.

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