RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

November 1977

Translated from *Uspekhi Khimii*, **46**, 1905-1928 (1977)

U.D.C. 93/99;54

Soviet Chemistry After Sixty Years

The six decades after the October Revolution have been a period of exceptional, progressive, and large-scale development of chemical science and practice in our country. An extensive network of scientific establishments, institutes, scientific centres, and chemical laboratories, attached to the Academy of Sciences of the USSR, the Academies of Sciences of the Union Republics, Ministries, Departments, Higher Educational Establishments, and directly in industrial undertakings has been created.

All the main fields of chemical science have developed vigorously: physical, organic, inorganic, and analytical chemistry. New branches of chemistry have arisen at the boundaries between these fields and also at their boundaries with other fundamental sciences—mathematics, physics, and biology. There has been an exceptional change in the characteristic features of chemical laboratories following the introduction of physical research methods. The Party and the Nation willed the construction and operation of a very large number of modern chemical undertakings.

During the years of the Second World War, Soviet chemists spared no effort to supply explosives, powder, ammunition, motor fuels, lubricating oils, steels, alloys, and medicines for the need of the Front and the National Economy.

At the XXVth Congress of the CPSU the General Secretary of the Communist Party of the Soviet Union, Comrade L. I. Brezhnev, assessed highly the role and importance of fundamental and applied research, the integration of science with industry, and the introduction of new scientific ideas into practice in the National Economy.

An effective system of coordination of scientific research in all branches of knowledge, including chemistry, has been created in our country. The authority of chemical science has been raised still higher and its role in scientific and technical progress, which is the basis of the powerful economic and defensive potential of our Motherland, has been defined.

An important place has been assigned to chemistry in the combined programmes for scientific and technical progress and its socioeconomic consequences during the period 1976–1980. Chemists should make a large contribution to the solution of the problems formulated by the Party for the Xth Five Year Plan. The combined processing of chemical raw materials (ores, petroleum, coal, shale, peat, gas, and wood), a further increase in production by the chemical and petrochemical industries (mineral fertilisers, chemical plant protection agents, plastics, synthetic rubber, chemical fibre and thread, dyes and paints, and the products of low-tonnage chemistry) and the manufacture of highly effective drugs are perhaps the most important among these problems.

A basis has been established for the creation of waste-free chemical manufacturing undertakings whereby chemical industry would genuinely and to an increasing extent cease being a factor with an unfavourable influence on the environment.

The methods of training of highly qualified cadres of chemists within the system of the higher and intermediate specialist education are being improved.

Scientific and technical relations with foreign countries concerning chemical science and practice have been intensified and placed on a concrete practical basis.

On the threshold of the seventh decade of the progressive development of the Soviet state, Soviet chemists, researchers, and practical workers confidently announce their complete readiness to solve the enormous number of specific problems, making thereby a necessary contribution to the prosperity of our Motherland.

The developments in chemistry in our country during the past sixty years since the Great October Revolution are outlined briefly below.

Physical Chemistry

A characteristic feature of the period after the October Revolution has been the rapid penetration of the theoretical and experimental methods of modern physics into virtually all branches of physical chemistry. Considerable progress has been achieved as regards the principles and methods of applied chemistry on the basis of the development of physical chemistry. New methods of carrying out chemical reactions, new continuous catalytic processes, and methods for the rational control of chemical reactions have been introduced into industry and chemical cybernetics has been developed. Important technical problems, such as the creation of methods for the formation of dispersed materials, the conversion of chemical energy into electrical energy, and problems of radiation-chemical synthesis have been solved with the aid of the physical chemistry of surface phenomena, electrochemistry, and radiation chemistry. Physical chemistry has also been important in the field of polymers.

Chemical physics—the science of the physical foundations of chemistry—a new field of natural science at the boundary between physics and chemistry whose subject is the study of the fundamental problems of the structure and transformation of substances, has been created.

Quantum Chemistry and Experimental Study of Molecular Structure

Much attention has been devoted to the physics of the elementary chemical step in reactions of inorganic and organic substances. A new field has been developed in the theory of the electronic structure of molecules, which deals with the interaction between the motions of electrons and nuclei. A method has been developed whereby relativistic effects can be taken into account in calculations on compounds with heavy atoms.

The important role of vibrationally excited molecules in chemical kinetics has been demonstrated. The kinetics of non-equilibrium processes occurring at high temperatures and in a high vacuum (for example, in the upper layers of the atmosphere) have been examined theoretically. A general theory of tunnelling processes in the kinetics of chemical reactions has been developed. A quantum-chemical basis has been created for the multiplet theory of catalysis.

The theory of directed valencies and valence states of atoms in molecules has been developed.

A theory has been created, whereby account may be taken of the interaction of electrons in systems with conjugated bonds and their spectroscopic properties can be explained.

Quantum-chemical methods of calculation have become effective instruments in the study of molecular structures and computer calculations on electron shells have come to be used on a large scale. Computer programs for calculations on chemical compounds have been developed. Numerous calculations on the electron shells of many specific molecules have been carried out by approximate quantum-chemical methods.

The role of quantum-chemistry in chemical research continues to grow. At the same time problems of molecular structure have been solved experimentally using numerous modern physical and physicochemical research techniques.

Combined computer systems have been created for the solution of structural problems; instruments have been designed for the analysis of complex conformational equilibria. An automatic coupled diffractometer-computer system has been developed for X-ray diffraction analysis. In order to investigate the structures of inorganic molecules at temperatures up to 2500°C, a new method of high-temperature gas electron diffraction is used. An X-ray spectroscopic apparatus using synchronous emission from opposed beams has been devised.

Chemical Kinetics

One of the greatest contributions of Soviet scientists to world science is the creation of a general theory of chain reactions. This theory combined and explained many facts on the basis of the idea of a complex set of elementary processes involving free atoms and radicals as the active centres of chain reactions. The theories of branched chain chemical reactions devised by Soviet investigators and numerous experimental studies based on it are of particular importance.

A new class of chain reactions with energetic chain branching has been discovered and investigated in detail; here branching takes place as a result of the vibrational energy of the excited species formed in exothermic elementary chain-propagation stages. An important application of branched chain reactions with energetic branches has been the creation on their basis of the first chemical lasers.

Numerous studies have been made on the detailed mechanism of chemical reactions (the elementary stages have been determined and the intermediates have been identified, including free radicals, atoms, ions, and complexes).

Various specific experimental methods have been developed for the investigation by ESR of active species, particularly free radicals and atoms.

In the study of elementary gas-phase reactions, the shock tube method has been widely used recently. The The dynamic characteristics of elementary reactions are being investigated by the method of crossed molecular beams. A maser method for the measurement of kinetic constants of the reactions of paramagnetic atoms and radicals in the gas phase and on the surface has been developed. A "positronium" method has been created for the investigation of the kinetics of fast chemical reactions in gaseous and condensed phases.

A fundamentally new phenomenon—the influence of the magnetic field on the rate of a chemical reaction—has been observed.

Extensive studies have been made on the kinetics and mechanism of the liquid-phase oxidation of organic compounds as a basis of many technological processes for the synthesis of valuable oxygenated compounds.

The kinetics and mechanisms of heterolytic liquid-phase processes have been investigated, the theory of acids and bases has been developed, and research has been carried out on the kinetics of topochemical reactions.

Thermal Explosion, Combustion, and Detonation

The theory of thermal explosion in exothermic reactions has been formulated and developed in studies by Soviet scientists and theories of flame propagation and detonation have been created. Research has been carried out on the combustion of fuel in engines. The kinetics of the decomposition, combustion, and detonation of condensed explosives have been studied on a large scale. The mechanism

of the detonation of explosives under impact has been discovered and the principle governing the conditions of a steady detonation has been formulated. The mechanical action of the shock wave has been studied and the results of research on spherical detonation have been applied in seismic prospecting.

A new method has been developed for the synthesis of refractory compounds (metal nitrides and carbides) directly in the combustion wave—"self-propagating high-temperature synthesis". A new form of the propagation of the centre of a chemical reaction—the spiral motion of the centre of combustion on the surface of the specimen—has been investigated.

Low-Temperature Chemistry

A new promising field—the chemistry of low temperatures (cryochemistry)—has been developed. It has been observed that individual chemical reactions (polymerisation, halogenation, and hydrohalogenation of olefins) take place at high rates at a temperature of about 77 K. The possibility of the occurrence of chain reactions in the solid phase (hydrohalogenation and nitration) has been demonstrated. Reduced temperatures and complex formation increase the selectivity of processes and the purity of the desired product.

Low-temperature photochemistry and a cryochemical technology for the synthesis of many valuable chemical compounds have been developed.

Homogeneous Catalysis

Numerous studies have been carried out on homogeneous catalysis—the most important method for increasing the selectivity of chemical processes. The compositions and geometrical and electronic structures of unstable intermediate complexes have been investigated. It has been shown that the maximum selectivities are attained in catalytic reactions of substances within the coordination sphere of the metal.

The discovery of the catalytic fixation of small molecules (CO_2 and N_2) has been a major achievement. The stereospecific catalysis of the polymerisation of dienes by π-allyl complexes of transition metals has been discovered. Studies on homogeneous catalysis, designed to simulate enzymatic catalysis, are being developed.

Heterogeneous Catalysis

In the field of heterogeneous catalysis, Soviet scientists discovered many effective industrial catalytic systems. Catalysts have been proposed for hydrogenation and dehydrogenation, for the synthesis of butadiene, for the manufacture of sulphuric and nitric acids, epoxyethane, maleic anhydride, acrylic acid, etc. Catalysts in the presence of which two chemical reactions may be coupled in the same apparatus (membrane catalysis) have been discovered. The catalytic activity of zeolites of different compositions has been demonstrated.

The electronic theory of catalysis has been formulated in the USSR. The multiplet theory of catalysis, according to which the rate of a catalytic reaction is determined by the geometrical and energetic correspondence between the adsorbed molecule and the catalyst surface, has been created. The theory of active *ensembles* and the theory of the chain redistribution of bonds, used for the comparative analysis of the mechanisms of homogeneous, heterogeneous, and enzymatic catalytic reactions, have been developed. Numerous experimental and theoretical studies have been carried out on adsorption and catalytic processes.

The active centres on the surfaces of solid catalysts have been investigated and it has been concluded that the intermediate complexes and free-radical states play an important role in the mechanism of heterogeneous catalysis.

Macrokinetics, which involves studies on diffusion kinetics, physicochemical hydrodynamics, heat and mass transfer, and the theory of reactions in a fluidised catalyst bed in relation to heterogeneous reactions, have been developed. Macrokinetics combined with the kinetics of heterogeneous reactions constitute the scientific basis for design calculations on industrial reactors and for the mathematical simulation of heterogeneous catalytic processes.

Enzymatic Catalysis

Studies on the structure of enzymes and the kinetics and mechanism of the action of enzymatic systems, immobilised enzymes, and cells have been expanded. Numerous carriers for immobilised enzymes have been found—natural and synthetic organic polymers and inorganic adsorbents. Immobilised enzymatic systems have been created for the needs of the food and textile industries.

Gel-like catalysts containing immobilised metal complexes have been proposed for the chemical reactions of unsaturated hydrocarbons.

High-Energy Chemistry

Radiation chemistry has developed both as regards the solution of many practical problems (radiation-chemical ageing and stability of materials, problems of radiation protection, chemical dosimetry, and the use of radiation for the synthesis and processing of organic low-molecular-weight and high-molecular-weight compounds) and for theoretical problems (the study of the kinetics and mechanisms of elementary processes and the nature and properties of short-lived intermediates in radiolysis).

A theory has been proposed whereby the range of dose rates, doses and temperatures at which radiation-induced initiation is significantly more favourable than thermal initiation can be predicted from the known kinetic parameters.

The radiolysis of water and aqueous solutions has been studied in detail.

Flash photolysis apparatus has been devised for the direct investigation of the kinetics of reactions of short-lived species.

Chemical syntheses employing the high and specific reactivity of hot atoms, generated as a result of nuclear processes, have been studied.

The chemical reactions of positronium have been investigated: oxidation, substitution, conversion, etc. The kinetics and mechanisms of reactions involving atoms and chemical process intermediates with a lifetime of 10^{-7}–10^{-12} s have been studied in detail for the first time.

The principles of non-equilibrium chemical kinetics have been developed in the field of theoretical plasma chemistry. The mechanisms of the physicochemical

phenomena and processes in low-temperature plasma have been investigated. Many plasma-chemical processes have been introduced into industry.

The principles of molecular photonics—the science concerned with the set of interrelated photophysical and photochemical processes—have been elucidated. The phenomenon of energy transfer between triplet molecular states has been discovered, and the photochemistry of dyes and related compounds has been developed.

Extremely rapid photochemical processes (for durations down to 10^{-11} s), mainly electron transfer processes, have been investigated and studies have been made of the reactions of the electronically excited states of radicals. A quantitative theory of radiationless intra- and inter-molecular energy transfer has been created.

"Two-quantum" photochemistry and quantitative methods for the study of two-quantum processes are being evolved.

A new field is developing, namely laser chemistry—the chemistry of molecules in a vibrationally excited state. The photochemical effect of infrared radiation has been demonstrated and methods have been devised for the synthesis of many chemical compounds.

Studies are being prosecuted on preparative organic photochemistry and the industrial employment of photopolymerisation processes. The nature of the photochemical degradation of polymers and the specific features of photochemical reactions in polymeric matrices have been studied. Research is being carried out on photochromic systems in order to create media with an automatically varying transmittance. New classes of photochromic spiropyrans and polymeric materials have been synthesised.

A new field has arisen—the chemistry of shock waves. The phenomenon of polymerisation in shock waves has been discovered and polypeptides have been synthesised [by this method] from aminoacids. Diamonds and a wurtzite-like boron nitride, whose crystals are suitable for the manufacture of high-quality cutting instruments, have been synthesised by impact compression.

Electrochemistry

Many important theoretical and experimental studies have been made in the field of electrochemistry during the period of Soviet rule. The foundations of electrochemical kinetics have been laid. A relation has been established between the reaction rate and the structure of the electrical double layer and the concept of the zero-charge potential has been introduced. Methods have been developed for the investigation of the metal/solution interface and for the measurement of electrode capacitances with the aid of alternating currents and for the measurement of charging curves; a quantitative theory of the double layer and a theory of adsorption on charged interfaces have been evolved.

A quantum-chemical theory of the mechanism of the elementary step in electrode reactions and processes in the bulk of the solution has been devised and a general criterion of the quantum (sub-barrier) or classical behaviour of various species in homogeneous and heterogeneous reactions has been obtained. A theory of convective diffusion has been developed.

A new field of electrochemistry has been created—the electrochemistry of solvated electrons. The law of electron photoemission from metals into electrolyte solutions has been discovered, the processes at electrodes have been investigated, and new electrode materials have been developed.

A large contribution has been made to the development of high-temperature electrochemistry (processes in fused salts) and to the study of the structure of the electrical double layer at the interface between fused metals and electrolytes. Free radicals have been detected for the first time in molecular melts. A quantitative theory of electrochemical information convertors has been created.

Research on the theory of corrosion processes and on protection against corrosion has developed widely. The role of complex formation has been discovered and the involvement of water molecules in the electrochemical stages of the dissolution of active metals has been established experimentally for the first time; the effect of the inhibition of the electrochemical dissolution of iron, chromium, and chrome steels under the influence of an oxidant has been observed. Important results have been obtained in studies on metal corrosion inhibitors. A new principle of the formation of corrosion-resistant alloys by cathodic doping has been proposed.

New steels and alloys resistant to corrosion in the corrosive media employed in chemical industries, under marine conditions, and in a subtropical atmosphere have been developed. The possibility of predicting the rate of atmospheric metal corrosion from the results of accelerated corrosion tests and meteorological characteristics has been demonstrated. A theory of the formation of lustrous deposits in the electrochemical deposition of metals has been proposed and studies in the field of bioelectrochemistry have been developed for the first time. The role of proteins as molecular generators of electrical potentials has been demonstrated.

Chemical Thermodynamics

Important results have been obtained in the field of thermochemistry, the science of equilibria, the science of solutions, and physicochemical analysis. The thermodynamic properties of various substances and of the parameters of many processes have been treated systematically and the handbooks "Termodinamicheskie Svoistva Individual'nykh Veshchestv" (Thermodynamic Properties of Pure Substances) and "Termicheskie Konstanty Veshchestv" (Thermal Constants of Substances), comprising many volumes, have been published.

New methods have been developed for the measurement and calculation of thermodynamic quantities, particularly at high temperatures, which is important for non-ferrous metallurgy, the thermodynamics of heat resistant alloys, metal oxides, and semiconductor compounds. A system of methods for the calculation of the physicochemical properties of various substances, whereby one can calculate many physical and physicochemical constants from a limited number of experimental data (reference points), has been created.

A new phenomenon, involving the limited miscibility of gaseous phases, has been demonstrated and the solubilities of gases in liquids at high pressures have been studied. The problem of chemical equilibria in complex mixtures at high temperatures, which is important for many branches of engineering, has been elucidated and methods have been developed for thermodynamic calculations on combustion and explosion processes.

Studies have been made on the thermodynamic reversibility of polymer solutions. The thermodynamics of solutions are being investigated and a theory of the liquid state has been developed on the basis of ideas concerning the motion of the molecules of a liquid. The presence of

short-range order in liquids, resembling the similar order in crystals, has been demonstrated and a method has been devised for the investigation of the micro-structures of liquids and solutions.

The thermodynamics of the solvation of ions and the structure of electrolyte solutions are being studied, structural ideas being related to thermodynamic properties.

Liquids and Solutions

The fundamental results obtained in the study of pure liquids and solutions refer to the field of the thermodynamic analysis of the properties of solutions, the fractionation of liquids, and the development of a theory of the distillation of liquid mixtures.

A general classification of solutions has been devised and a statistical theory of liquids and solutions has been developed. A set of experimental and theoretical studies on non-electrolyte and electrolyte solutions have been carried out. A quantitative theory of the dissociation of electrolytes has been developed.

Liquid systems with hydrogen bonds and the thermal motion of molecules have been investigated. The problems of the energetics of solvation, the regularities in the energies of formation of ions, and the problems of the proton affinity and hydration of ions have been examined.

Adsorption and Chromatography

Soviet science has had major achievements in the development of a theory of adsorption phenomena and chromatography and also in the field of the scientific principles of industrial sorption techniques.

A large series of studies has been carried out on calculations of adsorption isotherms on model ideal-crystal adsorbents, based on the theory of intermolecular interactions and statistical thermodynamics.

A novel theory of equilibrium and non-equilibrium adsorption phenomena on real solid porous adsorbents has been developed taking into account their energetic and geometrical characteristics. The theory has been widely accepted and is the basis of adsorption techniques.

A rational classification of porous structures, which serves simultaneously as a classification of adsorption phenomena, has been proposed. The fundamental differences between adsorption on an important class of adsorbents—the so called microporous adsorbents—and smooth surfaces have been demonstrated. A quantitative theory of adsorption, which has come to be called the theory of the volume saturation of micropores, has been created for adsorbents such as activated charcoals, zeolites, and finely porous gels. This theory is important for the description of not only adsorption equilibria but also adsorption kinetics (the kinetics of adsorption in biporous structures).

Adsorption on non-porous but energetically inhomogeneous surfaces has been investigated and an electronic theory of adsorption on the surfaces of semiconductors has been developed. Advances have been made in studies on the adsorption of gas mixtures. A thermodynamic concept based on the profound physical analogy between adsorption equilibria in heterogeneous systems and osmotic equilibria in bulk-phase solutions has been developing fruitfully in recent years.

Studies in the field of the synthesis of adsorbents with specified properties (specified by the surface and porous structure) have been expanded. The results obtained made it possible to organise the industrial manufacture of zeolites, which have found very extensive applications in the chemical and petrochemical industries.

Chromatography, which was discovered in our country, has been most closely related to the science of adsorption.

Studies have been made on the statics, kinetics and dynamics of chromatographic processes, methods have been developed and justified theoretically for the separation of the lanthanide elements, and complex formation in the chromatographic process and the radiation stability of ion-exchange materials have been studied. New chromatographic methods have been developed (the adsorption-complex formation method, partition chromatography of inorganic substances) and chromatographic processes have been intensified (by high temperatures and pressure) and simulated. New automatic chromatographic apparatus has been devised.

Colloid Chemistry

The science of surface forces, of the structure of boundary layers of liquids, and of the cleaving pressure has been created. Adhesion and boundary friction and capillary and electrophoretic phenomena have been investigated. The thermodynamics and statistical physics of surface phenomena have been evolved.

The modern science of the stability of disperse systems has been created and a quantitative theory of the stability and electrolyte coagulation of hydrophobic sols has been developed.

The phenomenon of the facilitation of the disruption, deformation, and dispersion of solids by adsorption, as a consequence of the decrease of the surface energy of the boundary with a surface-active medium (the Rebinder effect) has been discovered; the molecular mechanism and the conditions for the manifestation of the effect on all types of solids and materials have been established.

The physical chemistry of aerodisperse systems is being developed. Quantitative methods have been created for the experimental study of the degree of dispersion of aerosols, their electrical properties have been investigated, and the characteristics of the behaviour of the disperse phase on the fibres of the filter have been elucidated. The conditions governing the formation and coagulation of smoke and mists, procedures for controlling these processes, and control methods and procedures for the elimination of suspended particles from gases have been investigated.

A new field of modern colloid chemistry has been created—physicochemical mechanics, which solves problems associated with ensuring the required structure and mechanical properties in a wide range of materials—natural disperse systems and disperse systems involved in a wide variety of technological processes.

A physicochemical theory of the solidification of mineral binders has been developed together with the optimum technology of their application in building materials.

In the field of the physical chemistry of surfactants, ideas concerning the existence of a series of fundamentally different mechanisms of their action, determined by the structure of the adjoining phases and surfactant molecules as well as the conditions governing their adsorption, have been developed.

Crystal Chemistry

Crystal chemistry has developed on the basis of the extensive employment of mathematical methods (theory of symmetry groups) and physicochemical and physical methods (thermodynamics, quantum mechanics). Various experimental techniques have been used widely—diffraction (X-ray diffraction analysis, structural electron diffraction, and neutron diffraction) as well as other physical research methods (electron microscopy, infrared spectroscopy, ESR, and NMR).

The crystal chemistry of silicates and other related mineral and synthetic substances has been developed. The structures of many natural silicates have been determined and a new class of silicate structures has been discovered. Contributions have been made to the solution of practical problems associated with the employment of minerals and the development of materials for modern engineering. In order to create heat-resistant, phosphor, laser, and other materials, crystal-chemical studies have been made on orthophosphates, metaphosphates, and particularly ultraphosphates.

The atomic structures of metallic alloys have been analysed. The structural types of hundreds of intermetallic compounds have been found and a correlation has been drawn between the structures and physicochemical properties of substances. The scientific principles of a systematic treatment of intermetallic structures have been evolved.

Structural studies have been made on semiconductors and materials with unusual electrical and magnetic properties.

The foundations of the stereochemistry of Group VIII transition metal complexes as well as complexes of rhenium, molybdenum, tungsten, and the lanthanides have been laid. Studies on complexes with multiply linked ligands as well as the analysis of the structural manifestation of the mutual influence of ligands in transition and non-transition metal complexes are of great theoretical importance. The fourth metal–metal bond in dinuclear and trinuclear rhenium complexes has been discovered.

Organic crystal chemistry has been developing successfully. The general characteristics of the structures of organic molecules in relation to their reactivity and new synthetic possibilities have been studied and relations have been established between the crystal structure (molecular "packing") and the physical and chemical properties of organic substances.

The study of the spatial arrangement of molecules in a crystalline substance has occupied an important place. The principle of close packing of molecules has been formulated and a systematic treatment of organic crystalline structures has been achieved.

Organic Chemistry

Soviet organic chemists have made a large contribution to the development of world organic chemistry. The first Soviet achievements are the results obtained in studies on the chemistry of acetylenes, allenes, and dienes, on the catalytic transformations of hydrocarbons, on the formation of synthetic rubber, on the chemistry of organophosphorous compounds, and on the chemistry of natural products (terpenes and terpenoids, alkaloids, and carbohydrates). All the principal fields of organic chemistry subsequently developed successfully and on a large scale.

Physical Organic Chemistry

The electronic theory of chemical structure has developed significantly. Relations between the characteristics of the valence state of the carbon atom and the parameters of chemical bonds have been discovered. In the field of organoelement chemistry, the characteristic features of the interaction of various element–carbon bonds with neighbouring unsaturated molecular fragments have been discovered. Studies have been made on the structural characteristics and chemical properties of non-benzenoid aromatic systems. Quantitative relations between the reactivity and structure of organic molecules have been established, the theoretical foundations of the description of the phenomenon of tautomerism have been extended, and new types of tautomeric elementotropic and metallotropic transformations have been discovered. Ideas have been formulated about processes involving the transfer of the reaction centre, in which a dual reactivity is clearly manifested.

The mechanisms of various molecular rearrangements have been determined and new isomerisation reactions of aliphatic and aromatic compounds under the conditions of homogeneous and heterogeneous catalysis have been observed. A rearrangement of cyclic conjugated polyene compounds, accompanied by the migration of double bonds, has been discovered and investigated.

Studies have been made on the mechanisms of substitution reactions involving carbon atoms in aliphatic and aromatic compounds. Scientific foundations have been laid for the control of the mechanisms and rates of these processes.

Methods have been proposed for the generation and investigation of the properties and reactions of active intermediates in organic reactions—radicals, radical-ions, carbenes, carbenoids, carbonium ions, and carbanions. The reactions of stable radicals, occurring without the involvement of their free valence, have been observed and rearrangements of radicals involving the migration of a chlorine atom, thiyl group, and a hydrogen atom have been discovered. Computational and experimental methods for the determination of the electronic structures of free radicals, carbenes, and other methods have been devised. The dependence of the rate of rearrangement of carbonium ions on the electron deficiency at the carbonium centre has been found. The limits of the theoretical description of equilibria with participation of carbanions have been expanded. The results of studies on active intermediate species permitted a qualitative and in some cases a quantitative description of complex organic reactions occurring with their participation and a significant expansion of the scope of synthetic organic chemistry. The development of the method of "ionic hydrogenation" of organic compounds, characterised by a high selectivity, and the development of new processes involving the use of carbenes and carbenoids, etc. may serve as examples of this.

Important results have been obtained in the study of the stereochemistry of organic molecules. Methods have been developed for the determination of the steric structures of molecules by various physical research techniques. Extensive information has been obtained on the stereodynamics of organic molecules. The influence of steric factors on reaction rates and the possibility of

altering the mode and rate of reactions under the influence of high pressure have been studied. Research on sterically hindered phenols led to the creation of new scientific principles for the selection and employment of stabilisers of organic materials.

During the last two decades, there has been a considerable expansion of the application of computational quantum-chemical methods and experimental physical methods—in the first place molecular spectroscopic and X-ray diffraction methods—in studies on physical organic chemistry. Extensive information has been obtained about the relation between the structures of organic molecules and their spectroscopic characteristics. Studies on the application of computer techniques to the solution of structural problems in organic chemistry have been expanded.

Organic Synthesis

The wide-scale development of synthetic organic chemistry in many respects promoted the creation of the manufacture of organic substances in the USSR (dyes, organic fertilisers, polymers, pesticides, drugs, etc.). Fundamental research has been carried out on the synthesis of aliphatic compounds, some of which has a direct bearing on the chemistry of hydrocarbons and petrochemistry. Substantial results have been obtained in the chemistry of acetylene derivatives, which led to the development of a method for the synthesis of numerous aliphatic derivatives containing multiple bonds as well as functional groups. Studies have been made on the telomerisation reaction and its numerous modifications. Telomerisation products have found applications in the synthesis of aliphatic acids and other functional derivatives of this series.

Mention should also be made of the research on the employment of β-chlorovinyl ketones in organic synthesis, on diene synthesis, and on the application of reactions involving the addition of radicals having functional groups to multiple bonds in order to synthesise a broad spectrum of aliphatic derivatives, etc.

In connection with the organisation and development of the dye and drug industries, numerous investigations have been carried out on the chemistry of aromatic compounds. New methods have been developed for the preparation of aromatic nitro-compounds and a new procedure has been discovered for the synthesis of aromatic diazo-compounds on an industrial scale. The azo-coupling reaction, which is a fundamental process in the synthesis of azo-dyes, has been investigated.

The mechanism of the sulphonation of aromatic compounds has been elucidated and a study has been made of the mechanism of the halogenation of aromatic compounds in an aqueous medium. An activity series has been proposed for halogenating agents and the reactivities of many alkylating agents in relation to aromatic compounds have been studied.

Radical substitution in aromatic compounds has been vigorously investigated and the mechanism and fundamental characteristics of homolytic arylation have been determined. A study has been made of radical arylation with the aid of organometallic compounds.

The chemistry of non-benzenoid aromatic compounds has developed vigorously and there has been a large scale development of the chemistry of heterocyclic compounds. A novel method for the synthesis of heterocyclic systems with a wide variety of structures has been devised on the basis of substituted β-chlorovinyl ketones. A general method has been proposed for the preparation of five-membered heterocycles from acetylenic epoxides.

Numerous studies have been performed on the chemistry of furan derivatives and the reactions of chloromethylfurans, methods for the preparation of nitrogen-containing heterocycles incorporating the furan ring, diene synthesis, and substitutive addition reactions have been investigated.

Methods have been developed for the preparation of furan derivatives (sulphonation with pyridine : sulphur trioxide and the synthesis of benzofurans) and pyridine systems. New methods have been proposed for the synthesis of pyrones and their reactions have been studied.

Novel methods have been devised for the alkylation of 1-aminopyridine and the foundations for the industrial synthesis of acridine have been laid.

Numerous studies have been carried out on the chemistry of thiophen (reactions involving substitution in the thiophen ring and synthesis of macrocyclic compounds on the basis of thiophen). The reaction involving heterodiene synthesis has been discovered and new methods have been developed on its basis for the synthesis of pyridine and furan derivatives.

In heterocyclic chemistry, studies have been made on electrophilic substitution reactions involving indole, pyridine, pyrimidine, and azodicinnoline derivatives and on the microbiological transformation of heterocyclic compounds.

A new type of rearrangement of nitrogen-containing heterocycles has been discovered; the oxidative nucleophilic substitution reaction has been elaborated, etc.

Heterocyclic compounds of practical importance have been synthesised. The synthesis of 3-indolylbutyric acid has been achieved and a new method for obtaining serotonin as well as azaindoles and quinuclidines has been devised. Studies have been made on the chemistry of heterocyclic azines and azoles (quinazolines, quinoxalines, phenoxazines, acridines, tetrazoles, benzimidazoles, etc.). The influence of the heterocycle and other substituents on the amine–imine tautomerism and the conformation of formazans have been determined.

Studies on heterocyclic compounds have to a large extent promoted the development of theoretical ideas in organic chemistry and the solution of problems involving the creation of new and practically important substances: pharmocological preparations, dyes, and intermediates in fine organic synthesis.

The Chemistry of Organoelemental Compounds

After the significant results obtained in the chemistry of phosphorus, research on the chemistry of organometallic compounds of non-transition metals, carried out in the 1930s, was of the greatest importance. This was followed by a period of an exceptionally vigorous development of organoelemental chemistry based on a close combination of the methods and ideas of organic and inorganic chemistry. New synthetic methods were developed and reactions of organometallic and organometalloid compounds of non-transition elements were investigated. Compounds with unusual valences were discovered, studies were made on the relation between dual reactivity and tautomerism, and a new field of tautomerism was discovered—metallotropy in keto–enol systems. Studies were made on the characteristics of the chemical behaviour of quasi-complex, 'onium, and sandwich compounds. Organomagnesium synthesis was investigated comprehensively and a universal method was found for the synthesis of organomercury compounds. Methods were developed for the interconversion of derivatives of various elements.

Studies on the chemistry of phosphorus, silicon, fluorine, boron, tin, lead, mercury, iron, magnesium, zinc, cadmium, aluminium, arsenic, and other elements have acquired considerable theoretical and practical importance. Scientific schools engaged in research on the chemistry of the corresponding organoelemental compounds were founded and the manufacture (including large-scale manufacture) of organoelemental compounds and materials based on them (tetraethyl-lead, organosilicon monomers and polymers, organophosphorus insectoacaricides, organoaluminium catalysts, organofluorine Freons and monomers for fluoro-polymers, organotin and organoboron compounds, and ferrocene products) was developed. Syntheses of oligo- and polyorgano-aluminosiloxanes were devised, unusual properties of silatranes were discovered, and a general method was developed for the synthesis of the metallatranes of Group IV elements. New reactions of organotin compounds were discovered.

The chemistry of ferrocene, its derivatives, and other π-complexes of transition metals, which have found particular applications as combustion regulators, heat and light stabilisers for polymers, dyes, components of homogeneous catalytic systems, electron-ion-exchange resins, and effective and non toxic drugs, has been developing vigorously. Layer compounds of graphite with transition and non-transition metals, which have proved to be effective catalysts of chemical reactions, have been obtained for the first time. The phenomenon of nitrogen and carbon dioxide fixation by transition metal compounds has been discovered and investigated.

New reactions and rearrangements of organoboron compounds have been discovered and studied. New unsaturated and cyclic coordination compounds of boron as well as unique skeletal structures—bora-adamantane and bora-protoadamantane derivatives—have been obtained. Research in the field of carboranes—a new class of stable electron-deficient polyhedral organoboron compounds with unusual properties—has been developing. Carborane derivatives serve as starting materials for the synthesis of thermostable polymers.

The main fields in the chemistry of organosilicon compounds are associated with the development of methods for the synthesis of monomers used in the preparation of polymers having specified properties: polysiloxanes with spirocyclic, spiroladder, and spirolinear structures, carbosilazanes, organosilicon–organoelement polymers, etc. Silatranes and silaolefins (a new class of compounds) exhibit a specific biological activity.

Methods have been developed for the synthesis of various classes of organophosphorus compounds and studies have been made on the reactions of phosphorus(III) compounds with electrophiles. The chemistry of unsaturated and heterocyclic nitro-derivatives of organophosphorus compounds and phosphazo-compounds has been developed. Research has been carried out on the stereochemistry, conjugation problems, tautomerism, and dual reactivity of organophosphorus and organothiophosphorus compounds. Theoretical foundations have been laid in the study of the selective action of organophosphorus insectoacaricides, permitting the specific synthesis of selective pesticides with a low toxicity for warm-blooded animals and leaving no harmful residues in the environment. Among organophosphorus compounds, important physiologically active substances, agents active in the fight against agricultural pests, defoliants, herbicides, substances controlling the growth and pollination of plants, drugs, oxidation inhibitors, extractants, complexones, resins, additives to lubricating oils, and valuable monomers have been discovered.

The chemistry of organofluorine compounds, which is of great practical importance (the synthesis of Freons, fluorine-containing plastics, surfactants, drugs, water- and oil-repellent impregnating agents, fire-extinguishing compositions, and monomers for the synthesis of polymers stable over a wide range of temperatures) has been developed. Studies have been made on the electronic structures and reactions of aliphatic and aromatic polyfluorinated compounds. Methods have been devised for the synthesis of fluorine derivatives of virtually all classes of organic compounds.

Studies on telomerisation and cotelomerisation processes have led to the development of methods for the synthesis of a wide variety of organic polychloro- and other substances, some of which have extremely important applications.

Methods have been devised for the synthesis of monomers to be used in the industrial manufacture of polymeric materials. For this purpose, paraffinic hydrocarbons and olefins, formed in the cracking and pyrolysis of petroleum, are subjected to oxidation by molecular oxygen, catalytic epoxidation by hydroperoxides and peracids, oxidative ammonolysis, catalytic dimerisation and oligomerisation, hydrogenation and isomerisation in the presence of organometallic complexes, etc. Industrial processes have been created for the synthesis from a petroleum raw material of valuable products such as synthetic fibres and rubber, surfactants, fat substitutes, detergents, solvents, de-emulsifiers, synthetic protein mass, and the products of paint and varnish, pharmaceutical, and perfume industries.

Bio-Organic Chemistry

The development of bio-organic chemistry in the USSR has led to many important results. The chemistry of biologically important atypical peptides has been created and a method has been discovered for the synthesis of linear and cyclic peptides and depsipeptides by reactions involving the incorporation of amino- and hydroxyacyl groups in peptide systems. Peptide-protein antibiotics have been discovered and investigated (gramicidin S and actinoxanthine) and the structures of a number of glycopeptides have been determined. Combined research is being carried out on protein-peptide bioregulators, including hormones, antibiotics, neurotoxins, etc. The structures of certain hypophyseal hormones have been determined, the total synthesis of human insulin has been achieved, and technical rules have been developed for the industrial manufacture of oxytocin and angiotensin. More than twenty new neurotoxins have been investigated and the aminoacid sequences of five of them have been determined; the total synthesis of acylated α-bungarotoxin has been achieved.

Studies on polypeptides and proteins by physical methods have been expanded: infrared spectroscopy, optical rotary dispersion, and X-ray diffraction, in combination with theoretical calculations. Studies have been made on the structures and biological roles of enzymes and the mechanisms of enzymatic reactions. The catalytic function of myosin in the hydrolysis of ATP has been discovered, a relation has been established between respiration and the biosynthesis of ATP, and the transamination of aminoacids has been discovered.

The aminoacid sequences in the α-subunits of the DNA-dependent RNA-polymerase and aspartate aminotransferase and the steric structures of pepsin and many other

enzymes have been determined. The aminoacid–nucleotide linkages have been investigated in model compounds and nucleoproteins. Methods have been developed for the determination of the primary structures of oligonucleotides, their chemical and enzymatic syntheses, and their cross-linking into polynucleotide blocks, as well as methods for the chemical modification of nucleotides and nucleic acids.

In the field of carbohydrate chemistry, numerous studies have been made on the degradation and oxidation of cellulose and other polysaccharides. The structures of starch, amyloses, glycogens, dextrans, etc. and the mechanisms of their reactions have been investigated. Studies have been made on mono- and oligo-saccharides and compounds simulating glycopeptides. Methods have been developed for the synthesis of higher saccharides, deoxy-sugars, and *C*-glycosides, as well as new methods for the formation of the glycosidic linkage. A mass-spectrometric method has been devised for the determination of sequences in oligosaccharides. Studies have been made on the structures of many polysaccharides in microorganisms and algae. The structures of one of the most complex glycoproteins (the group components of blood) and of a number of glycolipids have been partially determined.

The chemistry of lipids is being elucidated. Methods have been devised for the synthesis of unsaturated aliphatic acids, new types of minor components of lipids have been discovered, and the characteristics of the structures of lecithins in tumour tissues have been determined.

Methods have been developed for the total synthesis of steroids. The total synthesis of corticoid hormones based on solasodine has been achieved. The industrial manufacture of steroid hormones based on cholesterol has been established in the USSR and the microbiological transformations of steroids have been investigated.

The chemistry of antibiotics, vitamins, and coenzymes has been developed, the antibiotic chloramphenicol has been discovered, and its structure and those of its derivatives have been determined. A synthesis of cycloserine has been developed and the mechanism of its action investigated. The configuration of tetracyclins has been established and their total synthesis achieved. Carminomicins and streptothricins have been investigated and modern industrial manufacture of antibiotics has been established.

Methods have been devised for the synthesis of many alkaloids—pilocarpine, curare analogues, emetine, etc. The industrial manufacture of drugs—both natural products and their derivatives and synthetic compounds—has been initiated.

Petrochemistry

The composition and properties of petroleums and their hydrocarbon and heteroatomic components have been studied. The characteristics of the distribution of hydrocarbons belonging to different groups (methyl-substituted and iso-prenoid alkanes, cycloalkanes with different numbers of rings and different types of ring junctions in the molecule, and polycyclic hydrocarbons) in petroleums and condensates have been determined. Numerous individual sulphides (thia-alkanes and thiacyclanes) and a number of mercaptans and thiophens have been synthesised and characterised, the characteristics of sulphur-, nitrogen-, and metal-containing (porphyrins) compounds in petroleums from different deposits have been obtained, and practical methods have been proposed for the isolation and utilisation of individual groups of sulphides and thiophens.

Studies on the refining of sulphur-containing petroleums (hydride desulphurisation, complex formation, etc.) have led to the creation of new methods for increasing the quality of petroleum products. The properties of various petroleum fractions, shale tar, and natural gas as starting materials for the microbiological industry have been investigated.

Studies have been made on the kinetics, chemistry, and mechanism of the pyrolysis of individual hydrocarbons and their mixtures. The nature of the fundamental elementary stages of the process has been determined and a mathematical model for the pyrolysis of mixtures of hydrocarbons and intensified methods for the pyrolysis of petroleum products have been proposed.

The reactions of individual hydrocarbons, their mixtures, and technical reactions on aluminosilicate catalysts as well as the chemistry and mechanisms of these reactions have been widely investigated. Methods have been developed for the catalytic and hydrogenation cracking, and new effective catalysts, including filled zeolites promoted by lanthanides, have been prepared. The scientific foundations for the industrial plasma-chemical processing of petroleum raw materials yielding acetylene, ethylene, hydrogen, $CO–H_2$ mixtures, carbon black, etc. have been laid.

Fundamental research has been carried out on the catalytic transformations of petroleum hydrocarbons leading to the formation of highly effective and selective catalysts for practically important processes involving the hydrogenation, dehydrogenation (of butane to butadiene, of ethylbenzene to styrene, etc.), and dehydrocyclisation of n-alkanes, the hydrodealkylation of alkylbenzenes, and alkylation, dimerisation and oligomerisation, disproportionation, isomerisation, co-oligomerisation, etc. These catalysts and the corresponding reactions have served as the scientific basis for specific syntheses of the required hydrocarbon structures from the most readily available hydrocarbons (ethylene, propene, butadiene, etc.) and have served as a basis for processes involving the formation of the most important monomers for the industrial manufacture of polymeric materials.

The conversion of petroleum hydrocarbons into their functional derivatives (oxidation, hydration, carbonylation, halogenation, ammonolysis, etc.) has been widely investigated in order to elucidate the kinetics and mechanisms of these reactions and to find new catalysts and reaction pathways. Industrial processes for the synthesis of intermediates (alcohols, acids, esters, nitriles, amines, halogenohydrocarbons, etc.) from petroleum raw material as well as valuable products with technical applications such as synthetic rubber and fibres, surfactants and detergents, plasticisers, lubricants and additives, flotation agents, synthetic foodstuffs, and fat substitutes were ultimately synthesised.

High-Molecular-Weight Compounds

A tendency to treat the science of polymers as an independent branch of chemistry combining in a single whole ideas about the pathways and characteristics of the synthesis of high-molecular-weight compounds, their properties, and the properties of materials made up of macromolecules arose in the 1930's. The studies and generalisations achieved by Soviet scientists have played a significant role in the development of the methodology and the fundamental

concepts of this new scientific field. The first practically important achievement was the development of the first ever effective method for the synthesis of butadiene rubber and subsequently the industrial application of this material.

Fundamental research on polymerisation processes has also developed successfully: a free-radical mechanism of polymerisation initiated by organic peroxides was demonstrated for the first time, the very concepts of initiation and chain transfer were formulated, and the most important kinetic relations were derived; these served as a basis for the regulation of the length of macromolecules in their synthesis by polymerisation methods. The discovery of oxidation-reduction initiation served as a foundation for the industrial processes involving the synthesis of rubbers by emulsion polymerisation.

A significant contribution has been made to the development of the modern kinetic theory of radical polymerisation in bulk and in solutions and the statistical theory of polymerisation has been developing successfully, in the first place for finding the relation between various possible mechanisms for the formation of macromolecules and their molecular weight distributions. Methods have been devised for controlling radical polymerisation, based on the use of complex-forming agents, which may strongly influence the reactivity of the monomers and radicals and alter thereby the selectivity and rate of reaction. The synthesis of macromolecules on synthetic polymer matrices, simulating matrix biosynthesis, has been achieved for the first time. Detailed studies have been made on solid-phase polymerisation also in other systems containing mutually ordered monomer molecules and anomalously rapid (compared with the usual liquid-phase processes) growth of polymer chains during phase transformations in solid monomers and when the latter are acted upon by a shock wave or on shear deformation under high hydrostatic pressures has been observed.

Important results have been obtained in studies on ionic and coordination-ionic polymerisation. At the end of the 1940's, the formation of "live" active centres in the sodium-initiated polymerisation of butadiene was demonstrated for the first time; important characteristics of the mechanism of similar polymerisation processes without chain termination were established later. Detailed studies have been made on the mechanisms of coordination-ionic polymerisation in the presence of complex organometallic catalysts, as a result of which the large-scale manufacture of stereoregular rubbers was established.

The stereospecific catalysis of the polymerisation of dienes under the influence of π-allyl complexes of transition metals has been discovered and investigated and the chain mechanism of the polymerisation of cyclo-olefins with ring opening and the carbene mechanism of reactions of this type were demonstrated. 1,4-*cis*-polyisoprene has been synthesised for the first time. In the field of ionic polymerisation of heterocyclic monomers, a new elementary step has been discovered—chain transfer with dissociation, and the polymerisation of ϵ-caprolactam has been studied.

A large series of studies has been performed in the field of polycondensation. New ways of synthesising polymers have been developed (polyrecombination, dehydropolycondensation, polytransarylation, and condensation cyclotrimerisation). A whole series of new polymeric materials, including thermostable polymers which are important for modern engineering, has been obtained as a result.

Important achievements have been made in the field of synthetic chemistry and technology of organoelement and particularly organosilicon polymers. Polyorganosiloxanes have been obtained for the first time. The fundamental principles of the synthesis of polymers with inorganic main chains, including polyorganometallosiloxanes, were developed subsequently and thermostable organosilicon polymers and oligomers, which have found very extensive practical applications, have been obtained. Polysilahydrocarbons—a new class of organosilicon polymers—have been discovered.

The development of a statistical theory of the reactivity of polymer chain units, taking into account the effect of neighbouring groups, has been important for the elucidation of the principles of the modern chemistry of macromolecules. The relations between the properties of graft and block copolymers, on the one hand, and their supermolecular structure and the structure of the component macromolecular units, on the other, has been deduced for the first time and the foundations have been laid for the structural-chemical modification of polymers. Methods have been devised for the radiation-chemical modification of polymeric materials by grafting monomers from the gas phase and the characteristics of the radiation-induced degradation and the radiation-chemical transformations of high-molecular-weight substances have been investigated. Studies have been made on the main characteristics of the vulcanisation of natural rubbers and cured rubber mixtures; the influence of topochemical factors in vulcanisation processes on the mechanical properties and operational characteristics of vulcanised materials has been demonstrated. Studies on a wide variety of possibilities in the chemical modification of cellulose led to the creation of many materials of practical value on the basis of this most important natural polymer. The problems of the degradation and stabilisation of polymers are being successfully elucidated; the significant role of structural-morphological factors (the supermolecular structure) in chemical degradation processes has been demonstrated.

A significant contribution has been made to the field of liquid-crystal polymers, polymers with a conjugation system, pharmacologically active polymers, and polymers for medical purposes, as well as polymeric systems stimulating various functions of biopolymers, specific catalysis, the self-agglomeration of ordered aggregates of complementary macromolecules, selective permeability (membranes), etc.

The kinetic concept of the vitrification of high-molecular weight compounds has played a fundamental role in the study of their physical properties. Subsequently this concept was developed into a system of ideas concerning the three physical states of amorphous polymers, determining the temperature and time intervals during which they can be processed and used on a rational basis. Studies of the relation between the physicochemical properties of polymers and their structure at the molecular and supermolecular levels led to the discovery of effective methods for the structural-physical modification of plastics, natural rubbers, and fibres. The general scientific principles of the physicochemical (structural) mechanics of polymeric materials have been developed. The concept of the thermofluctuation nature of the decomposition of polymeric materials has been formulated and experimentally justified. The characteristics of the flow of polymers have been investigated and a general treatment has been devised. The phenomenon of chemical flow (i.e. flow via the mechanically activated dissociation of macromolecules followed by recombination of the resulting macroradicals) has been discovered; new procedures for the manufacture of articles (procedures of the cold

stamping type) are being devised on the basis of this phenomenon. Ideas about the mechanisms of molecular and supermolecular plasticisation have been developed.

Studies on the relation between the structure and properties of synthetic raw rubbers and the operational characteristics of the cured rubbers based on them and research in the field of rigid very strong reinforced compositions have found important practical applications.

The demonstration of the thermodynamic reversibility of polymer solutions (the demonstration that they are true solutions) has been important for the creation of a general physicochemical theory of such solutions. Theoretical and experimental approaches to the determination of the conformational characteristics of individual macromolecules in dilute solutions have been developed and the first quantitative molecular theory of the conformational state of polymer chains and subsequently the modern rotational-isomeric theory of the flexibility of macromolecules have been created.

INORGANIC CHEMISTRY

Modern inorganic chemistry constitutes the basis for the formation of materials with specified properties, which are essential for scientific and technical progress, and for the effective employment of natural resources. Individual branches of inorganic chemistry are being developed—the chemistry of metals and alloys, non-metals, silicates, and light elements, coordination chemistry, radiochemistry, etc. On the basis of the achievements in these sciences, modern technological processes, control and regulation methods, and methods for the protection of the environment from contamination are being devised and incorporated in the national economy.

Fundamental research in the field of inorganic chemistry is being developed on a wide scale. This is promoted by the application in organic chemistry of the methods and achievements of physical, organic, and analytical chemistry, quantum-mechanical ideas, and computer calculations.

Coordination Chemistry

Fundamental studies have been carried out on the structures and reactivities of coordination compounds and the characteristics of the mutual influence of ligands have been investigated. The ring rule has been formulated—the phenomenon of the greatest stability for Chugaev's five- and six-membered rings.

The phenomena of the *trans*-influence of ligands have been discovered and their non-directional influence has been observed. The mutual substitution of ligands in coordination compounds, the redistribution of ligands and the dismutation of mixed compounds have been discovered in relation to uranyl compounds.

Many new coordination compounds of noble and rare metals, uranium and transuranic elements, lanthanides, and actinides with numerous ligands of different classes have been synthesised. Their compositions, structures, and stereochemistry have been investigated. A quantum-chemical theory of the bonds in coordination compounds has been developed. Methods have been devised for the extraction and refining of valuable elements on the basis of the formation and properties of their complexes.

Coordination compounds are used in the formation of catalytically active materials, high-purity metals, and materials for quantum electronics, microelectronics, and other applications in modern engineering.

Complex formation has become the basis of many analytical methods. Earth sciences (geochemistry, mineralogy, and petrography) have become a new field in which coordination chemistry has found applications. The mechanisms of the formation of the ores of non-ferrous and rare metals and minerals have been studied on the basis of coordination-chemical concepts. The transport of the majority of metals in natural waters has been shown to occur in the form of coordination compounds. Ideas have been formulated concerning the transport mechanisms and the mechanisms of the formation of uranium, tin, etc. deposits. Various methods for the subterranean "leaching" of the ores of certain rare and non-ferrous metals have been developed and used.

Coordination chemistry has found extensive applications in the study of biological processes—photosynthesis, respiration, and transport through membranes. The important contribution of coordinate bonds to the structures of nucleic acid and proteins has been demonstrated. The phenomenon of the chemical fixation of atmospheric nitrogen by complexes has been discovered.

A new field (biocoordination chemistry) has been developed, the properties of biologically active complexes have been investigated, and new drugs have been synthesised.

Many organophosphorus compounds, which behave as strongly coordinated ligands for rare, non-ferrous, noble, and radioactive metals and are used as effective extractants, have been synthesised.

Coordination compounds have found applications as catalysts in the chemical and petrochemical industries.

Radiochemistry and the Chemistry of Radioactive Elements

The problems of the isolation, concentration, and purification of radioactive elements have been solved. The distribution of radioactive microcomponents between the liquid and solid phases during cocrystallisation has been studied. The law of the isomorphic coprecipitation of radioelements has been formulated. The analogous law of distribution between a gas and a solid phase has been discovered. Distribution of radioactive substances between two liquid phases has been studied.

The general rules governing the solubility of actinides and fission elements have been discovered and new methods for the isolation and determination of thorium, cerium, zirconium, etc. have been found and introduced into analytical practice. A group method for the chromatographic separation of fission products on cation-exchange resins has been developed. Methods and conditions have been devised for isolation by extraction of individual radioelements from uranium blocks, for the extraction and refining of uranium and other elements from concentrates and industrial waste, for the separation of lanthanide metals, for the separation of actinides from lanthanides, etc. The behaviour of transplutonic and fission elements in aqueous organic media and the characteristics of the extraction of transplutonic elements by various synergistic mixtures have been studied. Extraction kinetics have been investigated, theoretical ideas in this field have been developed, the rates of extraction have been studied experimentally in many systems, and the observed features have been used in the solution of prac-

tical problems. A mathematical equation describing the rate of extraction of transuranic elements and other elements by various extractants under different regimes and conditions has been derived. New highly effective technological extraction processes for the isolation of all the individual lanthanides in a state of high purity have been developed and introduced into practice.

The fundamental rules in the sorption of radioisotopes have been established. A quantitative theory of adsorption on polar crystals has been created and chromatographic methods have been developed (ion-exchange, complex-formation, partition, and paper chromatography).

The results obtained in the chemistry of complex compounds are used for the analytical determination of uranium, thorium, radium, and mixtures of lanthanides, actinides, etc. Methods for the control of the manufacture of nuclear materials have been devised and new reactions involving organic reagents for the spectrophotometric determination of actinium, plutonium, americium, and curium have been proposed. [Computer] programs taking into account simultaneously many parameters (the half-life, the irradiation and cooling time, the standard, etc.) have been formulated. The laws of the physicochemical behaviour of substances under the conditions of extreme dilution have been established. Soviet scientists have made an important contribution to the prediction, study, and synthesis of new transuranic elements.

The properties of transuranic elements and their compounds have been studied and their compounds, including those of actinides in the extreme valence state, have been synthesised. Methods have been devised for the determination of the chemical nature of new elements. Research has begun on the synthesis and investigation of volatile organic derivatives of transplutonic elements. The first of these compounds (americium-phthalocyanine) has been synthesised and its stability and solubility have been investigated.

Hydrogen-free methods for the isolation of technetium-99, a method and procedure for the isolation of technetium-95, a procedure for the isolation of promethium-147, and methods for the fixation of isotopes on porous silica fibres in order to prepare radiation sources have been proposed.

The chemistry of the radioactive isotopes of the inert gases has been established as an independent discipline and problems of their isolation and storage are being solved.

The radioactive tracer method, widely used in the study of technically important materials and processes, has been developed.

Radioactivation analysis, which is highly specific and makes it possible to determine trace amounts of impurities in materials for the construction of reactors and rockets and for semiconductor engineering, in meteorites, etc. has been devised. A series of studies on the radiochemical determination of the contents of the cosmogenic ^{26}Al and ^{22}Na isotopes in lunar regolite has been completed.

Radiochemical analysis has found extensive applications in geochemistry. New data have been obtained on the radioactivity of the Pacific Ocean, the forms in which various radioelements exists, and their distribution between surface waters, deep waters, and the biomass. Much attention has been devoted to the problem of the contamination of the environment by radioactive materials, the storage of waste, the estimation of radioactivity near atomic establishments and dosimetric control, and the problem of the effect of small radiation doses on living organisms.

Fine Inorganic Synthesis

The syntheses of compounds of light elements, the so called high-energy compounds, have been extensively developed. Methods have been devised for syntheses in a low-temperature plasma by photochemical mechanisms and under the influence of laser radiation and pulsed and static pressures. Numerous aprotic solvents have been proposed.

Higher oxygen compounds of light elements (perchlorates, chlorine and nitrogen oxides, and alkali metal peroxides, superoxides, and ozonides), simple complex hydrides of light metals (boron, beryllium, aluminium, lithium, and sodium), the fluorides of non-metals (nitrogen, oxygen, chlorine, and other halogens), and the fluoro-cations based on these compounds have been synthesised.

The syntheses of inert gas compounds have been achieved. In view of their high oxidation potentials, these compounds are used as reagents in chemical and medical practice, in geology for the digestion of minerals, and in atomic power engineering for trapping the radioactive xenon and radon isotopes.

The Chemistry of Metals and Alloys

The modern technology of the production of metals and alloys has been established—steel and cast iron, light aluminium- and magnesium-based alloys, the alloying components of steels and alloys (copper, zinc, lead, cadium, tin, and antimony—for electrical engineering; tungsten and vanadium—in solid alloys for cutting instruments), precious metals, etc. using plasma, vacuum, and laser techniques. Methods have been developed for the plasma purification of metals. The characteristics of the physicochemical interactions in alloys and the properties of solid solutions have been investigated. A theory has been developed for and studies have been made on X-ray electronic and X-ray spectra and the electronic structures of inorganic crystals have been calculated.

Silicate Chemistry

The scientific principles of the production of cement have been elucidated. The formation and transformations of cement clinker, the hydration and hardening of cement, and the relation between the structure and composition of cement and its properties have been investigated. Studies have been made on the kinetics of the fundamental processes in the technology of cements by simulating the latter and a quantitative theory of clinker formation and the setting of cements has been created.

The technology of the production of special cements has been developed: very strong, rapid-hardening, hydrophobic, plasticised, barium-containing, expanding, and others. Methods have been devised for calculations on the vibrations of crystals with complex structures and the interpretation of the infrared spectra of silicates and their organosilicon analogues and a relation has been established between their structural and dynamic characteristics.

The chemistry of glass and the high-temperature viscous flow and solidification of glass have been investigated and a theory of the vitreous state has been devised. A new technology of sheet glass and glass-enamel heat resistant coatings has been developed.

New Inorganic Materials

Much attention has been devoted to the solution of the problems of the combined processing of minerals, the formation of new inorganic substances, and the synthesis of materials with specified properties. Methods are being developed for the synthesis of new inorganic materials, their structures are being investigated, relations between structure and properties are being established, and problems associated with the improvement of the quality of known materials are being solved.

The chemistry of the solid state has been developed and a general theory of the specific synthesis of solid compounds has been devised in order to create effective materials for modern engineering. The structures of inorganic compounds and the characteristics of the mechanisms of solid-phase reactions have been studied. The chemistry of semiconducting materials has been developed, the problems of the extensive purification of materials for the synthesis of semiconductors have been solved, and a technology has been developed for their preparation. A number of criteria whereby one can predict the presence of semiconducting properties have been proposed. New compounds having these properties have been synthesised.

A new field has been created—the chemistry of chalcogenide glass-forming compounds; these glasses have already found applications in xerography, silver-free photography, infrared optics, memory cells, and optoelectronics.

Instruments of a fundamentally new type, in the first place magnetic memory devices, have been constructed on the basis of chromium chalcogen-containing derivatives combining magnetic, electrical, and optical properties. Methods have been developed for the synthesis of magnetic semiconductors and for the growing of large and perfect single crystals. A theory of the doping of semiconductors has been devised. Methods have been developed for the analysis of their composition.

Studies have been made on the properties of oxide materials and the mechanisms of their electrical conduction. New materials for electrodes and magnetohydrodynamic generators have been made on their basis. Inorganic compounds which are promising for the electrovacuum industry have been obtained.

Important results have been achieved in the chemistry of materials for lasers, masers, and paramagnetic amplifiers. Special methods have been developed for growing crystals and for the synthesis of crystals with uniformly distributed impurities, and the industrial manufacture of the necessary compounds has been initiated. New materials for quantum electronics, particularly for the construction of chemical lasers and lasers based on liquid and vitreous media, are being sought.

The chemistry and properties of refractory heat-resistant, and thermostable materials is being investigated. Numerous compounds of different classes exhibiting thermal stability, high hardness, chemical resistance, etc. have been obtained by the method of self-propagating high-temperature synthesis (SHS). The possibility of SHS processes in metal–hydrogen systems has been discovered and many transition metal hydrides have been synthesised for the first time.

A series of studies on the chemistry of nitrogen-containing boron hydrides, clathrate compounds, in particular clathrate compounds of graphite with high-energy fluorine-containing oxidants, oxygen-containing tungsten and molybdenum compounds, complexes with oxidants and reductants within a single molecule, new types of solid solutions, etc., has been carried out. The fundamental characteristics of the chemical structures and properties within the classes of compounds already investigated have been determined for the specific synthesis of new compounds with predetermined properties.

Methods have been developed for the preparation of refractory filamental single crystals free from dislocations and possessing an improved strength and heat resistance.

ANALYTICAL CHEMISTRY

Analytical chemistry—the science of methods for the identification of chemical compounds and the principles and methods for the determination of the chemical compositions of substances and their chemical structures—has developed comprehensively in the USSR. The general trend in the development of Soviet analytical chemistry consists in an increasing role of instrumental analytical methods.

Extensive fundamental research has been carried out in different fields of analytical chemistry. The mechanisms of numerous analytical reactions, ionic equilibria, and complex-formation processes in analytical systems have been investigated, a theory of the separation and concentration of substances, particularly extraction, coprecipitation, and chromatography has been created, and micro- and ultramicro-analyses have been developed.

Methods have been devised for the analytical determination of individual elements and inorganic and organic compounds. A large contribution has been made to the development of the analytical chemistry of rare, scarce, and platinum metals.

Numerous new highly sensitive analytical methods have been devised, including X-ray spectroscopic microanalysis, drop analysis, microcrystalloscopy, and thin-layer chromatography. Kinetic methods have been devised.

Electrochemical methods—potentiometry, polarography and amperometry, coulometry, conductimetry, electrophoresis, and electrolysis—have been developed. Spectroscopic analytical methods—emission, atomic-absorption, and luminescence procedures—are being extensively developed and utilised. Numerous photometric methods using organic reagents and complexes have been devised.

Studies on the theory of the action and utilisation of organic reagents occupy a leading position. Methods have been devised for the analytical utilisation of non-aqueous solutions.

A large contribution has been made to the study of mineral raw materials in the USSR and analytical methods for ores and minerals have been developed and improved. Methods have been devised for the determination of valuable metals and scarce elements. Procedures for the control, including automatic control, of technological processes in various branches of industry, primarily in the basic chemical industry, in the metallurgy of ferrous, nonferrous, and rare metals, electronics, and pharmaceutical industry, have been developed. Non-destructive procedures based on emission spectroscopic and X-ray fluorescence analyses using quantum counting have been devised for rapid analyses in the metallurgical industry. Physical methods, particularly atomic-absorption spectroscopy, have been proposed for the determination of microimpurities in steels and alloys. Phase analysis is used to investigate the structures of steels. Chromatographic analysis has been developed for petrochemical purposes.

The industry of specially pure substances has been developed. The problems of the creation of special methods for the determination of the purities of substances in materials have been solved.

Following the start of space research, special methods involving X-ray procedures, Mössbauer and emission spectroscopy, and radioactivation analysis have been devised for the analysis of extremely small amounts of materials—the soil, atmosphere, and rocks of the moon and the planets.

Analytical chemistry has found applications in those branches of science and the national economy which deal with objects of plant and animal origin. Methods have been developed for the detailed analysis of soils and the analytical chemistry of pesticides. A procedure has been devised for the determination of protein in biological objects. Highly effective procedures for monitoring the state of air and water, whereby minute concentrations of harmful impurities may be detected, have been introduced. A method has been proposed for the simultaneous spectroscopic determination of up to 14 elements in the atmospheric dust of industrial cities with a sensitivity of 2×10^{-7}–1×10^{-6} g. Routine analyses of surface fresh water, sewage, waste water from industrial undertakings and public utilities, subterranean water, and sea water have been organised. A norm has been established for more than 500 components in the fresh waters of the USSR.

The extensive application of mathematics to analytical chemistry has begun, the statistical treatment of results has been initiated, and information theory is being used in the development of the metrological foundations of chemical analysis, the principles of experimental design are being developed, computer calculations are being introduced, and hybrid "analyser-computer" devices are being created. Such devices are being introduced in the analytical laboratories for ferrous metallurgy.

In connection with the reconstruction and intensification of ferrous metallurgy, the need for rapid analysis has grown. The smelting of steel in the oxygen-converter industry nowadays takes 15–20 min and its regulation requires information about the contents of carbon, sulphur, phosphorus, and other elements in the melt during the process. The solution of this problem required the wide-scale introduction of mathematics and automation into analysis.

Numerous modern analytical devices have been constructed; these include gas chromatographs, polarographs, spectrophotometers, mass spectrometers, and others.

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For obvious reasons, this outline is extremely fragmentary. No doubt there are also gaps and non-uniformities in the description. Nor has it been possible to name our research chemists to whom the high level of chemical science in the USSR is due. However, even a simple list of the problems considered, the theories and methods devised, the discoveries made, and the results obtained clearly demonstrates the gigantic contribution of Soviet chemists to world science.

Academician N. M. Emanuel'