RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

May 1974

Translated from *Uspekhi Khimii*, 43, 745-834 (1974)

U.D.C. 93/99; 54

Chemistry in the USSR Academy of Sciences

N.M.Emanuel'

Chemistry as a scientific discipline originated in our country at the time of the first Russian Academician in Chemistry, Mikhail Vasil'evich Lomonosov. As early as 1741 Lomonosov gave a completely modern definition of this science: "Chemistry is the science of the changes occurring in a compound body because it is compound". About 130 years later D. I. Mendeleev, in "The Principles of Chemistry", wrote: "The immediate object of chemistry is to study the homogeneous substances whose combination produces all the bodies in the world, their interconversions, and the phenomena accompanying such transformations". Both definitions are profoundly dialectical, for they regard chemistry as the whole set of manifestations of the chemical form of transformation of matter.

In its usual sense chemistry has always been and remains the science of the substances, products, and materials necessary to man and of the methods for their extraction and manufacture.

However, the ways of studying the composition, structure, and properties of many millions of individual substances, of knowing the detailed mechanism of the immense number of reactions at an elementary, atomic-molecular level, controlling chemical processes, and obtaining end-products with specified properties are so complicated and multifarious that modern chemistry is most intimately linked with mathematics, physics, and biology.

The Soviet period of development in chemistry is characterised by exceptionally high rates of growth of the volume of scientific research and increase in the number of lines of scientific investigation. Chemical laboratories changed radically in appearance, periodically undergoing almost complete material and technical re-equipment owing to the widespread introduction of the experimental methods of modern physics, radioelectronics, computer technology. The present time is characterised both by a process of obliteration of the boundaries between physical, organic, inorganic, and analytical chemistry and by the birth of new branches of chemical science.

Chemical research is conducted in the Soviet Union by large bodies of scientists associated in institutes of the USSR Academy of Sciences and those of the Union Republics, institutions of higher education, industrial institutes, and factory laboratories.

In many fields Soviet chemistry occupies leading positions in world science and has good prospects for further development, thanks to the constant attention of Party and Government, expressed in the resolutions of the Twenty-fourth Congress of the Communist Party of the Soviet Union.

The present paper gives a brief historical sketch of the development of chemistry in our country, mainly in the USSR Academy of Sciences.

PHYSICAL CHEMISTRY

The development of physical chemistry was directly connected with its previous history. It began with M. B. Lomonosov, who proposed the term "physical chemistry" for that branch of science which "uses the principles and experiments of physics to explain what occurs in compound bodies during chemical operations".

In pre-Revolutionary times physical chemistry developed in Russia mainly in the universities (Moscow, St. Petersburg, Kazan, Kiev, etc.). The situation changed substantially during the Soviet period, when physicochemical investigations came to be widely conducted not only

in university centres but also in institutes of the USSR Academy of Sciences, as well as in several branch scientific research establishments.

The first institute having a physicochemical outlook was the Karpov Physicochemical Institute founded in 1918 by A. N. Bakh, who remained its director for three decades.

Chemical physics—the physics of chemical processes—arose during the 1920s in the Leningrad Physicotechnical Institute, directed by A. F. Ioffe. The creation of this branch contributed to the development, in the mid-1920s, of the principles of L. V. Pisarzhevskii's electronic theory of valency and the publication in 1927 of the monograph "Elektronnaya Khimiya [Electronic Chemistry]" by V. N. Kondrat'ev, N. N. Semenov, and Yu. B. Khariton. The USSR Academy of Sciences Institute of Chemical Physics, founded in 1931 and directed by N. N. Semenov, became a most important centre of kinetic investigations. During recent years diverse kinetic researches have been made in the Institute of Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences, especially on the reactions of combustion and also the study of the structure of coordinated metal complexes.

In 1945 the Laboratory of Colloidal Electrochemistry (founded in 1930 by V. A. Kistyakovskii) formed the basis for establishing the Institute of Physical Chemistry of the USSR Academy of Sciences, where work has been done on the problems of surface phenomena, the theory of chromatography, problems of corrosion, radiochemistry, thermodynamics, and colloid chemistry.

The study of the theory of electrochemical processes, in particular the electrochemistry of organic compounds, and problems of radiation and quantum chemistry and of hydrodynamics provide the subject-matter for the Academy's Institute of Electrochemistry, founded in 1958 by A. N. Frumkin.

The Institute of Catalysis of the Siberian Division occupies a leading position in the field of heterogeneous catalysis.

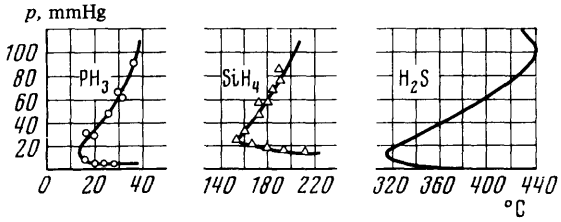


Figure 1. Regions of chain ignition of phosphine, silane, and hydrogen sulphide.

At the present time hardly any branch of chemistry and biochemistry is conceivable without the use of physicochemical methods for analysing and investigating chemical substances, their structure, and properties. Physicochemical investigations are therefore undertaken in almost all chemical institutes. Examples are the Institute of Organoelementary Compounds, in which the structures and reactivities of organic compounds are studied by infrared, nuclear magnetic resonance, and electron spin resonance spectroscopy, and the Institute of Organic Chemistry, where N. D. Zelinskii founded the theory of organic catalysis, later developed by his students, and where A. A. Balandin made his investigations on heterogeneous catalysis.

The Institute of Petroleum-chemical Synthesis, founded by A. V. Topchiev in 1958, studies the mechanism of many petrochemical and polymerisation processes, the physical chemistry of polymers, and in particular the rheology of polymers.

The Institute of General and Inorganic Chemistry (founded by N. S. Kurnakov) has become a centre for developing physicochemical methods of analysis.

Physicochemical methods of studying chemical reactions are widely used in the institutes of the Siberian Division of the USSR Academy of Sciences (Institute of Organic Chemistry), as well as in the Arbuzov Institute of Organic and Physical Chemistry (Kazan), in the Institute of Chemistry in Gorky, and in many other institutes of the USSR Academy of Sciences.

The oldest of the physicochemical institutes of the academies of Union Republics is the Pisarzhevskii Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, which is concerned with investigating radical reactions, polymerisation processes, and heterogeneous catalysis.

Chain Reactions and Elementary Chemical Processes

One of the greatest achievements of Soviet physical chemistry is the theory of branched chain reactions. At the end of the 1920s N. N. Semenov, Yu. B. Khariton, and Z. F. Val'ta discovered that phosphorus vapour ignited only when a certain critical oxygen pressure had been reached. Addition of an inert gas (argon) enabled ignition to be observed at oxygen pressures below the critical value. The existence of a "critical" diameter of the reaction vessel was also discovered. Semenov put forward the idea of branched chain reactions to explain the new facts. The reaction was assumed to be a chain process, with an increase in the number of free radicals occurring in elementary steps which were termed chain branchings. The progressive growth in the concentration of free radicals, under conditions such that the rate of chain branching exceeded the rate of chain termination, led to chain self-ignition (Fig. 1).

Chain ignition is an isothermal explosion. The evolution of heat in this process is insignificant, since the explosion is due to a progressive growth of the number of active centres. In subsequent years the work of many scientists has demonstrated the widespread occurrence of branched-chain reactions. It was Semenov who inferred that high concentrations of free radicals are formed in branched-chain processes.

In this connection a large number of determinations were made of the concentrations of free radicals in chain reactions. After several years V. N. Kondrat'ev had developed methods enabling free atoms and radicals to be studied while reaction was proceeding (line absorption and catalytic recombination methods). Hydrogen atoms and hydroxyl radicals were detected by these methods in the combustion of molecular hydrogen, and carbonyl sulphide in that of carbon disulphide. It was also discovered that SO free radicals were formed in the slow oxidation of hydrogen sulphide. The concentrations observed exceeded by many orders of magnitude the thermodynamic equilibrium concentrations under the experimental conditions.

In 1944 E. K. Zavoiskii discovered the remarkable phenomenon of electron spin resonance (e.s.r.). Research on its extensive use in chemistry was undertaken by V. V. Voevodskii and his students and coworkers. At the end of the 1950–1960s the latter worker collaborated with A. V. Nalbandyan in recording by e.s.r. the formation of hydrogen and oxygen atoms in the combustion of hydrogen, together with other free radicals (Fig. 3).

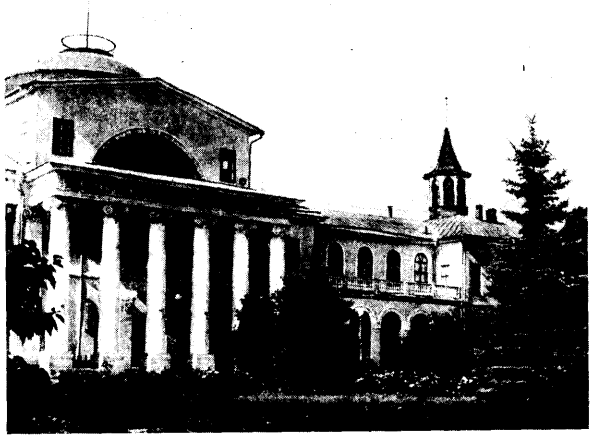


Figure 2. Institute of Chemical Physics of the USSR Academy of Sciences, main building.

Kondrat'ev used electron bombardment to examine the dissociation of species, and was the first to apply mass spectrometry to the investigation of chemical reactions. The mass-spectrometric method was later developed by V. L. Talroze, who also developed the method of the diffusion flame in a flow system for studying the gas-phase reactions of atoms with molecules in order to determine their rate constants. This method enables reactions to be studied in the absence of the wall effect of the reaction vessel.

The possibility of heterogeneous chain initiation was suggested in 1927 by M. V. Polyakov, and experimental proof of the occurrence of this important process was given in 1948 by A. A. Koval'skii using his method of separate calorimetry.

The next stage in the development of the theory of branched-chain reactions was the concept of degenerate branching (Semenov). Such slowly evolving branched reactions were assumed to involve formation of a comparatively labile intermediate, which had a certain probability of breaking down into free radicals. Examples of products causing degenerate chain branching are formaldehyde in the high-temperature oxidation of methane and hydroperoxides in the oxidation of organic compounds at 100–150°C.

Semenov put forward the hypothesis that free radicals may be formed in bimolecular interactions between saturated molecules. Experimental evidence was given by A. E. Shilov and F. S. D'yachkovskii for the interaction of triphenylmethyl chloride and ethyl-lithium: triphenylmethyl radicals, formed by the reaction

$$EtLi + Ph_3CCl \rightarrow LiCl + Ph_3C^{\cdot} + Et^{\cdot}$$

were recorded by electron spin resonance. Subsequently the possibility of occurrence of the reactions

$$RH + O_2 \rightarrow R^{\cdot} + HO_2,\ 2RH + O_2 \rightarrow R^{\cdot} + RO^{\cdot} + H_2O,\ ROOH + RH \rightarrow RO^{\cdot} + R^{\cdot} + H_2O$$

was established.

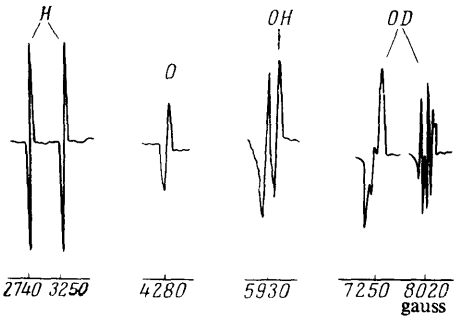


Figure 3. Electron spin resonance spectra of H and O atoms and OH and OD free radicals in the oxidation of H_2 and D_2.

Processes of this type proved to be especially characteristic of reactions involving molecular fluorine. Strong chemiluminescence in the visible region of the spectrum was observed by A. E. Shilov, L. Yu. Rusin, and A. M. Chaikin in the reaction

$$F_2 + HI \rightarrow F + HF + I$$

and this could be due only to formation of an electronically excited IF* molecule. Superequilibrium concentrations of atomic iodine were recorded by e.s.r. in this reaction. The method of diffusion flames was used to determine the rate constant both here and in the reaction of fluorine with hydrogen bromide.

Investigation of the chain reactions involved in the gas-phase fluorination of hydrogen, methyl iodide, methylene dichloride, etc. led Semenov and Shilov to the concept of energy branching—a new type of branched-chain reactions—in which excited molecules, capable of breaking down to form free radicals, were formed in chain propagation.

The reaction between hydrogen and fluorine is accompanied not only by the usual emission $HF^* \rightarrow HF + h\nu$ but also by stimulated emission, which reaches 1–2% of the energy of the chemical reaction. The duration of the flash of stimulated emission is 5×10^{-6} s, whereas that of chemiluminescence is 5×10^{-2} s (Fig. 4).

A recently developed laser, which uses the slow oxidation of hydrogen sulphide, is the first example of a chemical laser whose functioning is determined entirely by a set of elementary chemical reactions, and there is hardly time for the "leakage" of vibrational energy as a consequence of collisions during the emission.

Shock tubes began to be widely used during the 1960s. They were essentially ideal pulsed reaction vessels in which a rapid change of pressure heated the gas almost instantaneously to temperatures of the order of 1000° and even 10 000°C. A temperature pulse lasted for $(1-50) \times 10^{-4}$ s, and any surface effect was almost completely absent.

Studies were made of the elementary processes of the vibrational excitation and the dissociation of diatomic molecules—halogens, oxygen, nitrogen, and carbon monoxide (S. A. Losev)—and polyatomic molecules—hydrocarbons and nitro-compounds (A. A. Borisov, V. G. Knorre)—as well as electronic excitation and ionisation involving atoms and radicals (S. M. Kogarko and I. S. Zaslonko). Examination of the decomposition of ammonia and nitrous oxide showed directly the occurrence and the main features of "energy" chain processes, as well as the presence of critical conditions for autocatalysis due to the non-equilibrium distribution of the internal energy of the reactants. Vibrationally excited molecules N_2^V act as chain-transfer agents in the decomposition of hydrogen azide: their collisions with the initial molecules transfer vibrational energy to the latter by resonance, thereby increasing the rate of decomposition. Fig. 5 illustrates the shock tube with which G. B. Manelis and A. P. Genich studied the decomposition of ammonia.

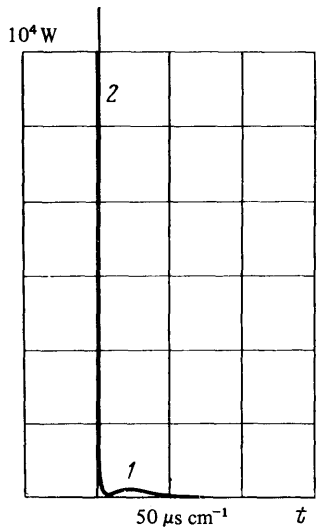


Figure 4. Intensity of chemiluminescence: 1) spontaneous; 2) induced (laser).

The development of ideas on a chain mechanism of the cracking of hydrocarbons and investigation of the kinetics and the mechanism of the elementary stages can be attributed to the work of V. V. Voevodskii and A. D. Stepukhovich.

The theory of the activated complex has been used to interpret the mechanism of a large number of elementary chemical reactions. Stepukhovich calculated the steric factors of many bimolecular reactions. E. A. Shilov and Ya. K. Syrkin introduced the concept of the formation of cyclic (four- and six-membered) transition complexes in bimolecular reactions.

V. I. Gol'danskii has recently made a detailed examination of the general theory of tunnel transitions in the kinetics of chemical reactions with a Maxwellian energy distribution of the interacting molecules. He obtained a criterion characterising the temperature below which tunnel transitions predominate over barrier transitions. A negative temperature coefficient of reaction velocity is shown to be possible because of quantum effects in barrierless transitions like inverse spontaneous predissociation. The recently discovered low-temperature quantum limit to the rate of chemical reaction in the radiation-induced solid-phase polymerisation of formaldehyde can be regarded as experimental confirmation of the possibility of sub-barrier transitions. The rate of growth of the polymer chain, induced by cobalt-60 γ-rays, was found to obey the Arrhenius law at 80–150°K, but strongly diverged from this law when the temperature fell further. At 10°K the experimental rate of addition of one monomer unit to the chain exceeded the extrapolated value by many powers of ten. It thus appeared that, instead of complete freezing of processes at temperatures close to the absolute zero, there was a measurable limiting rate of exothermic reaction, perhaps resulting from the increasing importance of tunnel transitions at extremely low temperatures.

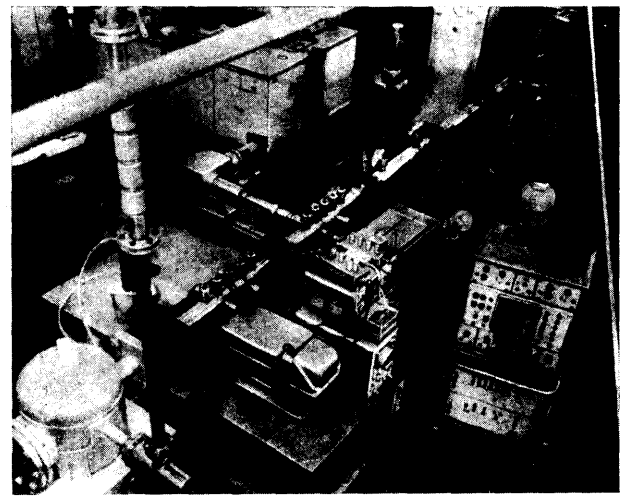


Figure 5. Equipment for investigating elementary chemical processes in a shock tube.

During recent years E. E. Nikitin has further developed the theory of the elementary acts of chemical reactions to describe the kinetics of non-equilibrium processes, which are important at high temperatures and under high vacua (e.g. in the upper layers of the atmosphere). His theory of the non-equilibrium decomposition of diatomic molecules takes into account the dependence of the probability of vibrational transitions on the vibrational quantum number. A general statistical theory of unimolecular reactions starts from the postulate that the total energy of an active molecule is redistributed statistically among active degrees of freedom, and it includes as a particular case all other theories of unimolecular reactions. N. M. Kuznetsov made theoretical calculations of vibrational temperatures and rate constants for the dissociation of certain small molecules under conditions of a non-equilibrium energy distribution. New experimental methods were proposed for studying the elementary acts of chemical reaction.

A widely used method for studying the mechanism of chemical reactions is to conduct them under ultra-high pressures, comparable with the internal pressure, when change of pressure leads to a change of the effective volume of the reaction. This enables hypothetical models of the activated complex to be tested. M. G. Gonikberg studied the effect of pressure on sterically hindered reactions and on polymerisation processes. Kinetic measurements in various solvents under high pressures have enabled the solvation of the activated complex to be studied.

Yu. N. Ryabinin suggested that the adiabatic expansion and compression of gases could be used to investigate the kinetics of fast non-isothermal reactions. Later this method was applied to the quantitative study of processes (the rate of cooling of the gaseous mixture reached 10^6–10^7 deg s^{-1}).

The rate constants of elementary reactions have been measured by means of a hydrogen maser. The method is based on measuring the reaction velocity from the change in the spin state of hydrogen on interaction of its atoms with non-paramagnetic molecules (Tal'roze).

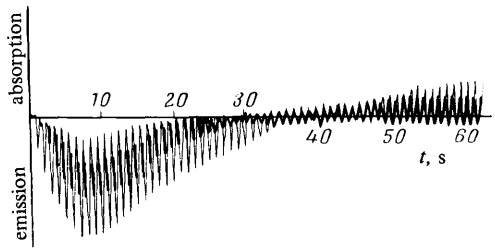


Figure 6. Kinetics of polarisation of the protons in nitrobenzene.

The mechanism of radical reactions can be investigated by studying the chemically induced dynamic polarisation of the product nuclei in a magnetic field. The basis of the method is that preferential orientation of the nuclear spins in the molecules of the products results from the occurrence of radical reactions in a magnetic field (chemically induced dynamic polarisation of the nuclei), and the nuclear magnetic resonance spectrum exhibits either abnormally large absorption or the emission of radio-frequency energy. Fig. 6 illustrates the kinetics of the variation of the n.m.r. signal (i.e. the kinetics of nuclear polarisation) obtained by A. L. Buchachenko and E. T. Lipmaa for the protons of nitrobenzene formed in the reaction of *p*-nitrobenzenediazonium tetrafluoroborate with sodium methoxide. A quantitative theory of dynamic nuclear polarisation was developed.

An interesting phenomenon was observed in the effect of a magnetic field on the proportions of the products of free-radical reactions. Thus the ratio of the yields of products obtained from the reaction of fluorobenzoyl fluoride with n-butyl-lithium changes by 37% on passing from the Earth's magnetic field of 0.5 to fields up to 25 000 oersteds (U. N. Molin).

Gol'danskii established a new "positronium" method for studying the kinetics of fast chemical reactions in gas and condensed phases. Rate constants of the formation of positronium atoms, as well as those of the excitation of electronic levels of the molecules, are determined by observing the lifetime of positronium and the intensity of the long-lived component in the annihilation.

The resolving power of a new method of microwave spectroscopy—the spin echo resulting from the action of modulated ultra high-frequency power (a series of short-lived pulses) on the specimen—exceeds that of the e.s.r. method by factors of 10–10^2 in the investigation of hyperfine interactions (Yu. D. Tsvetkov, D. G. Semenov).

Gol'danskii developed the application of γ-resonance spectroscopy to the investigation of chemical reactions. The use of Mössbauer spectroscopy enabled the rate of intramolecular electron transfer to be measured. The time of transfer in the radioactive transmutation of cobalt-57 in the compounds $^{57}Co^{II}_m[Fe^{III}(CN)_6]_n$ and $Fe^{II}_m[^{57}Co^{III}(CN)_6]_n$ was $(1-2)\times 10^{-8}$ s.

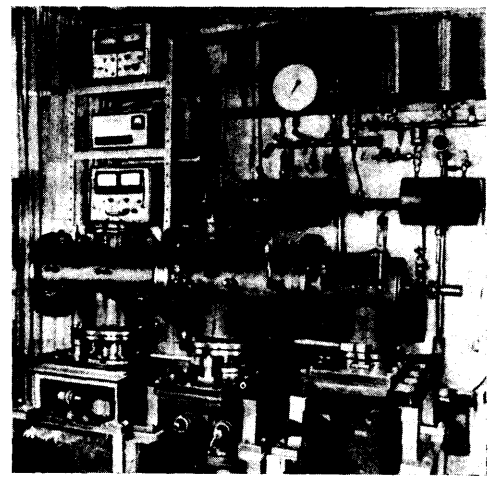


Figure 7. Equipment for studying elementary chemical reactions by the molecular beam method.

In connection with the practical importance of non-equilibrium processes the need arose for the experimental investigation of elementary reactions under conditions such that the chemical interaction of two species is an isolated process, unaccompanied by deactivation of the molecules or secondary chemical reactions, due to collisions with other molecules. Such conditions also provide new opportunities for examining the dynamics of the elementary act. Elaboration of such methods led to the design of apparatus with crossed molecular beams. Pressures of 10^{-6}–10^{-7} torr in the scattering vessel eliminate "background" collision of particles, since under these conditions any particle undergoes at most one collision in the scattering zone. The vacuum in the detector entered by the reaction products is maintained at 10^{-9}–10^{-10} torr. Fig. 7 illustrates equipment for the investigation of elementary processes in molecular beams.

Yu. B. Khariton and Ya. B. Zel'dovich worked out a chain theory of the fission of uranium.

Chain Reactions in the Liquid Phase

At the end of the nineteenth century A. N. Bakh put forward the peroxide theory of slow oxidation processes. This theory has been repeatedly confirmed in practice. During recent years kinetic methods have made it possible to extend ideas on the chemical mechanism of the liquid-phase oxidation of organic compounds. New types of elementary reactions have been discovered (in particular, new types of reactions of chain branching and chain initiation have been suggested), rate constants for various elementary stages have been measured, and processes of catalytic and inhibited oxidation have been studied quantitatively (N. M. Emanuel', I. V. Berezin, D. G. Knorre, E. T. Denisov, Z. K. Maizus, E. A. Blyumberg, V. Ya. Shlyapintokh, G. E. Zaikov, N. I. Mitskevich, R. V. Kucher, B. K. Zeinalov, and others). Heterogeneous reactions have been shown to play an important part in liquid-phase oxidations, just as in the gas-phase reactions. The effect of the solvent on individual elementary reactions has been established, and the roles of specific and non-specific solvation of the reactants in homolytic reactions have been established. Ideas on the catalysis of slow chain oxidations have been put forward and developed, and a procedure for gaseous initiation by "weak" radicals (ozone, nitrogen dioxide, etc.) is suggested.

V. Ya. Shlyapintokh and R. F. Vasil'ev studied the chemiluminescence accompanying oxidation. They showed that the chemiluminescence of hydrocarbon oxidations arises in the act of recombination of free peroxy-radicals. Measurements of chemiluminescence enable the radical-recombination rate constants to be determined (under non-stationary conditions), as well as the rate constants for the reactions of the radicals with molecules and with inhibitors of radical reactions.

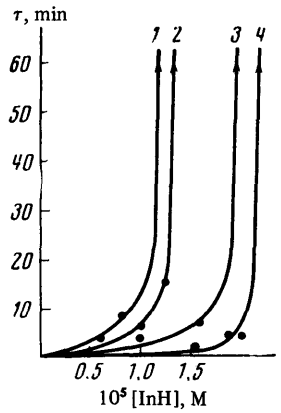


Figure 8. Dependence of induction period in the oxidation of ethylbenzene on the concentration of the inhibitors: 1) diphenylamine; 2) *N*-phenyl-2-naphthylamine; 3) 2-naphthol; 4) 1-naphthol.

The action of inhibitors on slow oxidations exhibited critical phenomena, indicating the branched-chain character of these processes (A. B. Gagarina) (Fig. 8). Study of the synergism appearing on the introduction of a mixture of inhibitors into an oxidisable medium suggested radical interaction of the inhibitors resulting in regeneration of the more effective inhibitor (G. V. Karpukhina).

The laws of liquid-phase oxidation in open systems were investigated as the scientific foundation for continuous processes in chemical technology (I. P. Skibida).

At the beginning of the present century N. A. Shilov put forward a theory of chemical induction. In his monograph on coupled oxidations he introduced the idea that chemical induction (the acceleration of a chemical reaction by another reaction taking place spontaneously in the system) is due to the formation of intermediates involved in both stages of the process. Shilov was in effect the first to draw attention to the fact that redox reactions are complicated multistage processes involving the formation of intermediate products.

The method suggested recently for the preparation of methyloxiran by oxidising a mixture of propene and acetaldehyde is based on the principles of simultaneous oxidation applied to slow chain reactions. The hydroperoxy-radical formed by oxidation of the acetaldehyde serves as epoxidising agent for propene.

A fertile application of kinetic methods has been to describe the development with time of several biological processes, such as malignant growth, aging, radiation sickness, and the action of chemical and physical factors in the environment on living organisms. Kinetic parameters have been revealed which permit the efficiencies of different methods for the therapy of malignant diseases to be evaluated quantitatively.

It has been discovered that the content of free radicals in tumour tissue increases during the initial period of growth. This relation is extremal: a maximum content of free radicals is observed before the tumour attains its maximum rate of growth. A group of compounds has been found which have an anticancer effect, which are able to diminish the scale of harmful effects of chemical contamination of the environment on the organism, which extend the life of experimental animals, and which possess radiation-protective properties. All these substances are inhibitors of free-radical processes.

Homogeneous Catalysis

One of the first investigators of homogeneous catalysis in Russia was E. I. Shpital'skii, who as early as the beginning of the present century developed the main theoretical concept of homogeneous catalysis—the formation of active intermediate products—and, in contrast to van't Hoff and Arrhenius, suggested that not one but several intermediate catalyst–substrate complexes were formed, differing in composition, stability constant, and reactivity (down to complexes that deactivate the catalyst). This theory later received convincing experimental support: intermediate products in the decomposition of hydrogen peroxide by molybdates and by tungstates (permolybdates and pertungstates respectively), etc. were isolated.

The formation of molecular complexes of compounds of metals of variable valency with hydroperoxides (in catalytic decompositions) and their role in catalysis have been confirmed quantitatively by S. K. Maizus and I. P. Skibida using kinetic and spectroscopic methods.

E. A. Shilov established that π-complexes have a decisive role as intermediate species in various reactions involving alkenes. In a study of acid catalysis (in particular by the Lewis acids—boron trifluoride, aluminium trichloride, etc.) N. M. Chirkov concluded that reactive intermediate

π-complexes of alkenes with hydrogen ions were formed. Ya. K. Syrkin and I. I. Moiseev examined the formation of π-complexes of palladium(II) chloride with alkenes in the preparation of aldehydes. These workers used phenomena such as synergism occurring in mixtures of several catalysts for the oxidation of ethylene to acetaldehyde in the presence of the palladium(II) chloride–copper(II) chloride catalytic system.

A. I. Shatenshtein proposed a new kinetic method for determining the strengths of very weak acids and bases (e.g. hydrocarbons), and traditional views on acids and bases were revised.

The study of metal-complex catalysis, which is closely connected with enzymic catalysis, began to acquire great importance during the 1950s. Organometallic (especially π-allylic) complexes are used as catalysts for stereospecific polymerisation (B. A. Dolgoplosk). Papers by L. A. Nikolaev and A. P. Purmal' reported studies of the mechanism of enzymic catalysis, investigation of the roles of ligand and metal in various types of reactions (the oxidation of ascorbic acid, the decomposition of hydrogen peroxide, etc.), and elucidation of the detailed chemical mechanism of catalysis.

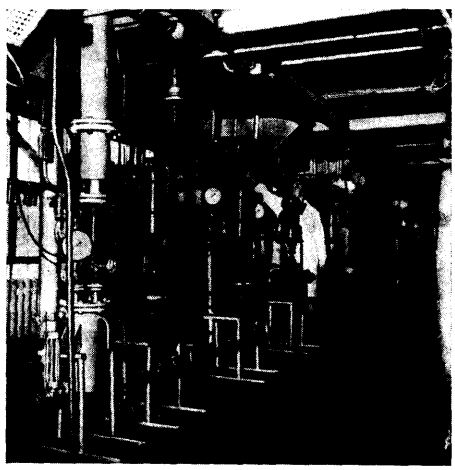


Figure 9. Pilot plant for synthesis of hydrazine from molecular nitrogen and water.

The problem of the catalytic fixation of small molecules—the activation of oxygen, nitrogen, carbon dioxide, and carbon monoxide by catalytic systems—has aroused interest recently. During the 1960s M. E. Vol'pin and A. E. Shilov discovered the catalytic fixation of nitrogen with the formation of hydrazine and ammonia (Fig. 9). Compounds of bivalent vanadium in the presence of magnesium salts form an effective catalytic system in alkaline and alcoholic aqueous media. The yield of ammonia and hydrazine increases with the ratio of magnesium to vanadium. The fixation of carbon dioxide by complexes of Group VIII transition metals has been studied.

When hydrocarbons and compounds of metals are oxidised together in organic solvents, conversion of the hydrocarbons (cyclohexane, alkanes) to alcohols is accompanied by a change in the valency of the metal.

A nevel type of catalysis—micellar catalysis—was discovered by I. V. Berezin. It consists in a marked change (by several powers of ten) in the rate of organic reactions in aqueous solutions under the influence of surface-active substances, as a consequence of solubilisation of the reactants by micelles of the surface-active compounds (Fig. 11).

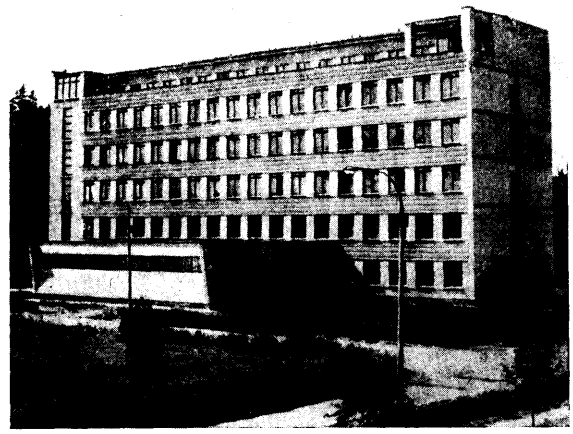


Figure 10. Laboratory building of the Department of Kinetics and Catalysis of the Institute of Chemical Physics of the USSR Academy of Sciences.

A paper by D. G. Knorre, L. G. Chuchukina, and N. M. Emanuel' established that a catalyst has a "dual function": at sufficiently high concentrations salts of metals of variable valency cease to exhibit catalytic properties, and the "catalysts" begin to inhibit the process. The dependence of the inhibiting properties on the composition of the chelate group, the redox potential, and the electron density on the central atom of the chelate has been studied, and the conversion products of the metal complexes have been isolated and examined.

Heterogeneous Catalysis

In the field of heterogeneous catalysis numerous papers have appeared on the selection of effective new catalytic systems. At the start of the 1920–1930s V. N. Ipat'ev began a comprehensive investigation of metal oxides as heterogeneous catalysts. N. D. Zelinskii discovered general-purpose hydrogenation and dehydrogenation catalysts such as nickel on alumina and platinum on carbon. In 1928 S. V. Lebedev proposed a mixed zinc–aluminium catalyst for the synthesis of butadiene from ethanol. The action of catalytic semiconductors, in particular germanium, was investigated (S. Z. Roginskii, O. V. Krylov).

Investigations of adsorption and chemisorption were very important in connection with the study of heterogeneous catalytic reactions. A theory of catalysis and chemisorption on non-uniform surfaces was elaborated (S. Z. Roginskii, O. M. Todes). A correlation between activation energy and heat of adsorption was established by M. I. Temkin. The principles of physical sorption on porous materials were studied by M. M. Dubinin.

Various methods were suggested for investigating the structure, properties, and activity of catalysts. Besides the usual X-ray diffraction, electron diffraction, magnetic methods, sedimentation analysis, and microweighing were introduced into practical heterogeneous catalysis.

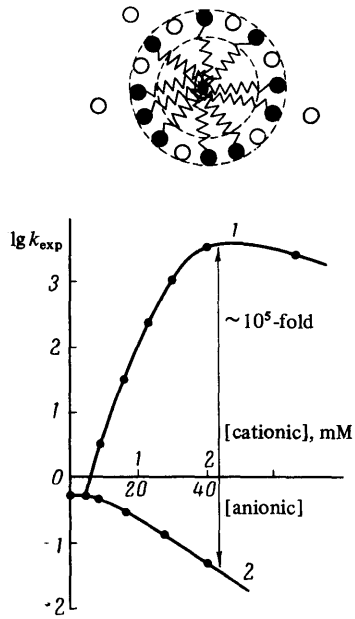


Figure 11. Formation of micelles (upper diagram) in micellar catalysis. Variation of acylation rate constant with concentration of surface-active agents: 1) cationic; 2) anionic.

A. M. Rubinshtein suggested determining specific surface from the adsorption isotherms of benzene or carbon tetrachloride vapour determined under dynamic conditions. The displacement of characteristic curves for a sorbed gas and measurement of the work of sorption of the gas (vapour) have been used to measure the specific surface of a catalyst (M. M. Dubinin and A. V. Kiselev). Various physicochemical methods (electrochemical and chromatographic) were used by A. A. Balandin and Kh. M. Minachev.

Kiselev calculated theoretically the energies of adsorption of complicated molecules on crystalline surfaces. A. N. Frumkin and A. I. Shlygin proposed to study the mechanism of hydrogenation from the charging curves for the catalytic electrodes. This made it possible to examine quantitatively the adsorption of hydrogen on the surfaces of metals (platinum).

Investigation of the properties of species adsorbed on a catalyst surface has been approached in earnest with the development of the most recent physicochemical methods. V. V. Voevodskii used electron spin resonance to study the structure of the active centres (radicals and ions), and showed their non-uniform distribution on solid surfaces. The O_2^- radical-ion adsorbed on a surface has recently been detected by γ-resonance (Mössbauer) spectroscopy (Fig. 12).

Kinetic isotope methods opened up great possibilities for investigating the mechanism of heterogeneous chemical reactions (S. Z. Roginskii, M. B. Neiman).

Balandin's multiplet theory of catalysis presupposes structural and energetic conformity between the crystal lattice of the catalyst and the molecule of the reactant. The formation of surface complexes involving active centres of catalysis (multiplets) is significant for catalysis. Physical adsorption on the catalyst surface is followed by movement of the molecule along the surface and formation of a multiplet complex at a certain orientation of reactant molecules and active centres. Bond redistribution in such a complex results in formation of the final products. Multiplet schemes, based on a large quantity of experimental information, explain almost all routes of catalytic conversion of hydrocarbons.

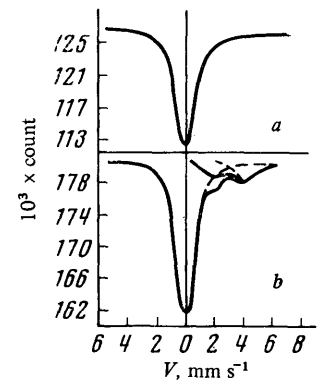


Figure 12. γ-Resonance spectra of tin–molybdenum catalyst (V = relative rate of movement of source): *a*) initial specimen; *b*) specimen after adsorption of oxygen and propene at 200 °C.

N. I. Kobozev applied a theory of active ensembles to deposited catalysts. It was based on the assumption that a certain number of catalyst atoms—not a single atom—was involved in catalysis. Such groups may be formed by the migration of atoms along the catalyst surface.

A large number of publications on aspects of the chemistry of heterogeneous catalytic reactions have appeared from G. K. Boreskov, K. V. Topchieva, V. A. Roiter, and others. Boreskov suggested that the activity of a heterogeneous catalyst should be measured by the rate of chemical conversion per unit active surface of the catalyst: i.e. he introduced the concept of specific catalytic activity. He examined the mutual influence of catalyst and substrate on the properties of the catalytic system, which may lead to a strong dependence of catalytic activity not only on the degree of conversion of the reactants but also on their initial concentration.

Roginskii proposed a new classification of catalysts linking the activity of a catalyst with the character of the interaction between catalyst and substrate. Catalysts were divided into two groups—electrical conductors (metals and semiconductors) and non-conductors (ionic crystals, gels). This classification has been tested on

many oxidation processes (S. Yu. Elovich, L. Ya. Margolis, G. M. Zhabrova).

L. V. Pisarzhevskii's electronic theory played an important part in establishing the theory of the elementary act of heterogeneous catalysis. It assumed that electrons of the catalyst took part in redox reactions. The modern form of the electronic theory of catalysis was formulated by F. F. Vol'kenshtein. Free electrons and holes of the semiconductor, acting as free valencies, are supposed to take part in chemisorption processes. The reactivity of a chemisorbed molecule depends on the form of the chemisorption (valency-saturated, radical, or radical-ionic form).

N. N. Semenov, V. V. Voevodskii, and F. F. Vol'kenshtein put forward a chain theory of heterogeneous catalysis based on the electronic theory and on their view of the role of heterogeneous factors in the formation and destruction of radicals. This theory assumes that reaction may occur on the surface of a heterogeneous catalyst by a chain mechanism. O. M. Poltorak has recently developed the concept of chains of redistribution of bonds, and used it for a theoretical analysis of diverse catalytic processes. It permits a unified approach to the mechanism of homogeneous, heterogeneous, and enzymic catalyses.

The work of A. A. Balandin, D. A. Frank-Kamenetskii, G. K. Boreskov, Ya. B. Zel'dovich, M. G. Slin'ko, O. M. Todes, D. V. Sokol'skii, G. I. Panchenkov, M. F. Nagiev, I. I. Ioffe, S. L. Kiperman introduced into practical heterogeneous catalysis methods for calculating the reaction order, rate constants, and activation energy of heterogeneous reactions in vessels with ideal mixing and displacement, examined the macrokinetics of reactions in a fluidised bed, and applied statistical methods to investigating the kinetics of heterogeneous reactions. The gradient-free methods of conducting chemical reactions (under conditions of ideal mixing) proposed by M. I. Temkin have been applied to such kinetic studies.

Various processes—dehydrogenation, dehydrocyclisation, hydrogenation, etc.—can be combined in the same apparatus as a consequence of the development of original membrane catalysts (V. M. Gryaznov, V. S. Smirnov).

The role of heterogeneous catalysts and the mechanism of their action in liquid-phase processes have been investigated in the oxidation and decomposition of hydroperoxides (E. A. Blyumberg, Yu. D. Norikov, Ya. B. Gorokhovatskii). The heterogeneous catalyst is shown to be involved in initiation, branching, and termination of the oxidation chain, and also to influence the way in which the hydroperoxide breaks down.

The catalytic properties of heterogeneous catalysts can be varied by donor–acceptor modification by means of gaseous additives.

Thermal Explosion, Combustion, Detonation

The theory of thermal ignition in exothermic reactions, formulated by N. N. Semenov and subsequently developed by his school, has been exceptionally important, both theoretically and practically. The nature of thermal ignition, resulting from the predomination of the evolution of heat over its removal from the system, is apparent in an exponential increase in reaction velocity with rise in temperature in the vessel and a corresponding temperature rise. The theory of thermal explosion was developed and refined by O. M. Todes and D. A. Frank-Kamenetskii. Conditions of ignition were determined for vessels of various geometrical shapes taking into account the thermal conductivity equation. These conditions enable flash points of various substances to be calculated with good accuracy.

The theories of flame propagation, detonation, and explosion limits were developed by Ya. B. Zel'dovich. Specific régimes of combustion were investigated by K. I. Shelkin, Ya. K. Troshin, et al., who showed that the rate of flame propagation was affected by the movement of the gas caused by expansion of the products of combustion. Investigations were made of the burning of light fuel in engines. On the basis of this work A. S. Sokolik and A. I. Voinov proposed a new mode of organisation of combustion in motors—fuel injection—which has been further developed by L. A. Gusak.

Kinetic studies of the decomposition of condensed explosives were begun in 1929 by S. Z. Roginskii. Together with Todes he elaborated a statistical theory of the kinetics of topochemical and crystallisation processes. Yu. B. Khariton and also A. F. Belyaev studied the kinetics of the breakdown of explosives. They revealed the mechanism of explosion after impact, and formulated the principle defining the conditions of persistent explosion. Belyaev's discovery that the combustion of explosives takes place in the gas phase, after they have vaporised, became widely known.

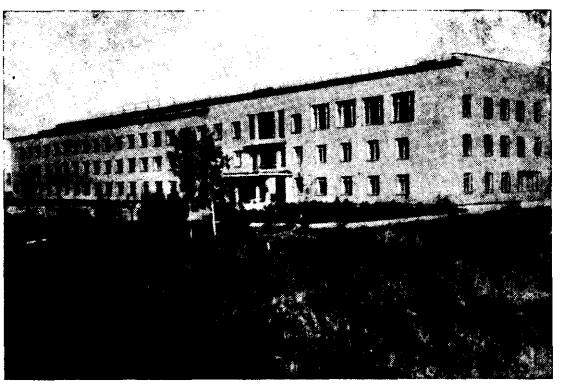


Figure 13. Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences.

P. F. Pokhil, A. Ya. Apin, A. A. Andreev, F. I. Dubovitskii, V. K. Bobolev, B. P. Zhukov, A. G. Merzhanov made many investigations of the mechanism of thermal explosion. M. A. Sadovskii studied the structure, mechanism of formation, and propagation of shock waves. The mechanical action of a shock wave in air was examined, and the dependence of the maximum pressure in the wave on the weight of the charge and the distance from the site of explosion was determined. Spherical detonation, which has found application in seismic exploration, was studied by S. M. Kogarko.

Merzhanov worked out a new method for obtaining refractory compounds (nitrides, carbides of Groups III–VI metals)—"self-propagating high-temperature synthesis"—and a new form of propagation of the seat of chemical reaction—a kind of spiral motion of the focus of combustion on the surface of the specimen—was studied. Reaction vessels have already been constructed which enable

considerable quantities of titanium carbide and molybdenum disulphide to be obtained (Fig. 14). A. N. Dremin showed that new crystalline modifications can be obtained by the action of powerful shock waves on various substances.

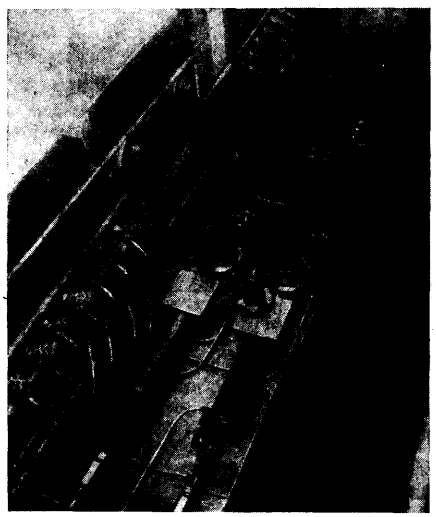


Figure 14. Equipment for the production of refractory inorganic compounds by "spontaneously propagated high-temperature synthesis".

High-energy Chemistry

This field of science is concerned with the kinetics, mechanism, and practical application of reactions in which the energies of individual atoms, molecules, and radicals exceed the energies of thermal motion and frequently the energies of chemical bonds. These result in peculiar new mechanisms of chemical reaction, which are improbable in equilibrium systems at ordinary temperatures.

Research on radiation chemistry began with the work of V. A. Kargin, V. V. Voevodskii, S. S. Medvedev, N. A. Bakh, and others. The theoretical principles of radiation chemistry are now being worked out: studies are being made of elementary processes in gas and condensed phases, of the nature and properties of short-lived intermediate products of radiolysis (solvated electrons, ions, free radicals, excited molecules), the kinetics and mechanism of radiation-chemical reactions in homogeneous systems, aspects of radiation polymerisation, problems of the radiation modification and radiation-chemical protection of various materials, etc.

Ion–molecule reactions of organic compounds have been discovered (V. L. Tal'roze), methods have been suggested and developed for the radiation cross-linking of polyalkenes and the modification of polymeric, porous, and other materials (V. L. Karpov, Kh. U. Usmanov, A. M. Kabakchi, E. E. Finkel', V. L. Tsetlin), and theories have been elaborated for the radiation-chemical oxidation of organic compounds (Bakh), gaseous and heterogeneous radiation-chemical reactions (S. Ya. Pshezhetskii), radiation polymerisation (A. D. Abkin, V. I. Gol'danskii, V. L. Tal'roze), and the radiolysis of water and aqueous solutions (P. I. Dolin, M. A. Proskurnin, B. V. Ershler, A. K. Pikaev, L. T. Bugaenko). Stabilisation of the hydrated electron has been detected in frozen aqueous solutions (Pikaev), and principles have been worked out for the chemical dosimetry of ionising radiations (S. V. Starodubtsev, A. M. Kabakchi).

The theoretical investigations have served as a basis for the development of applied radiation chemistry. Processes have already been worked out for obtaining a biodegradable sulphonate (R. V. Dzhagatspanyan), synthesising telomers of ethylene with carbon tetrachloride (A. A. Beer), and making polyheterosiloxane insulating tape and rubber–glass cloth (I. Ya. Poddubnyi et al.).

The unique phenomenon has been observed that the coefficient of dry friction is reduced by several powers of ten when non-metallic rubbing surfaces are exposed to a slight flux of short-range radiation (V. L. Tal'roze, A. N. Ponomarev, A. A. Silin, E. M. Dukhovskoi).

Experimental and theoretical research on low-temperature plasma constitutes a new sector of high-energy chemistry. General principles of non-equilibrium kinetics have been formulated, and its fundamental equations given (L. S. Polak, D. I. Slovetskii, Yu. A. Kolbanovskii). The scientific foundations of plasmachemical technology have been laid, its characteristic features being short reaction time (10^{-5}–10^{-3} s), high degree of conversion, pure products, and in several cases the accomplishment of difficultly realisable processes. Plasmachemical methods are used to prepare acetylene, pigment titanium dioxide, materials for microelectronics, and other products.

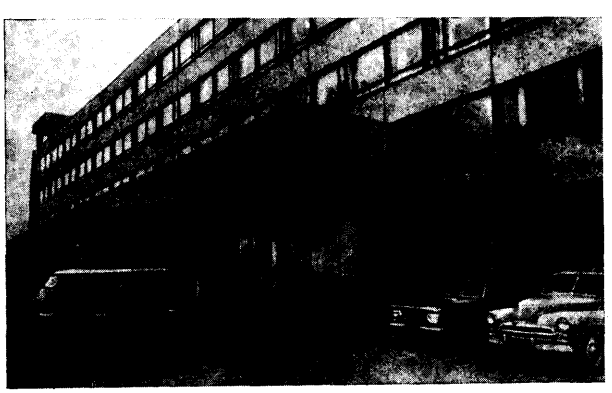


Figure 15. Radiochemical building of the Institute of Physical Chemistry of the USSR Academy of Sciences.

A shock wave provides a new method for stimulating and accomplishing chemical conversions: the chemistry of shock waves constitutes a new branch that studies the transformations of condensed substances resulting from percussive compression. These researches, started by Yu. N. Ryabinin, were developed by V. I. Gol'danskii, A. N. Dremin, P. A. Yampol'skii, S. S. Bogdanov, G. A. Adadurov, O. N. Breusov. High-pressure phases—diamond and wurtzite-like boron nitride (B–BN)—have been obtained by percussive compression. The latter has yielded especially durable polycrystals, suitable for the

production of high-quality cutting tools with the best available characteristics. Polymerisation has been observed, and the possibility shown of cross-linking macromolecules by the action of shock waves to form a three-dimensional network.



Figure 16. Linear electron accelerator of the Institute of Physical Chemistry of the USSR Academy of Sciences.

An important sector of high-energy chemistry is nuclear chemistry—investigation of the chemical consequences of nuclear processes (nuclear reactions, radioactive disintegration) and research on the chemistry of new atoms and the peculiar systems produced by the action of positrons and various mesons on matter. The high and specific reactivity of the hot species resulting from nuclear processes has been the subject of research by An. N. Nesmeyanov, A. N. Murin, V. D. Nefedov, B. G. Dzantiev, T. V. Tsetskhladze, and others. Methods have been found for the chemical stabilisation of hot atoms of tritium, carbon, nitrogen, sulphur, halogens, and certain metals in organic and inorganic media, in gas and condensed phases. The results open up new paths for the preparation of labelled compounds and for the concentration of radioisotopes.

Various types of chemical reactions of positronium have been studied, and the physical chemistry of the positron and of positronium has been established (V. I. Gol'danskii, V. P. Shantorovich). The foundations of the physical chemistry of muonium have been laid down in the works of V. G. Firsov, I. I. Gurevich, V. G. Nosov. Research has started on the chemistry of mesoatoms and mesomolecules (Yu. D. Prokoshkin, L. I. Ponomarev).

Photochemistry

The study of chemical reactions occurring under the influence of light is very important for the theory of chemical processes and for solving problems of photosynthesis, photoreception, photography, the photostabilisation of polymeric materials, etc.

P. P. Lazarev investigated the fading of dyes for the first time.

Fundamental photochemical researches were carried out by A. N. Terenin. His hypothesis of the triplet nature of the metastable states of organic molecules which are responsible for their phosphorescence has received much experimental confirmation. The properties of triplet states have been studied, and their role in various photochemical and photophysical processes has been revealed. The phenomenon of triplet–triplet energy transfer has been established (A. N. Terenin, V. L. Ermolaev). Flash photolysis was used by A. V. Karyakin and A. K. Chibisov to show the important role of the triplet state in photochemical redox reactions involving pigment and dye molecules.



Figure 17. Apparatus for studying radiation copolymerisation in the Institute of Physical Chemistry of the USSR Academy of Sciences.

The work of V. N. Kondrat'ev gave rise to study of the elementary act of interaction between light and matter. The mechanism of induced predissociation and energy-transfer processes was investigated. A. B. Nalbandyan studied the mechanism of the photochemical oxidation of hydrocarbons sensitised by mercury vapour and by chlorine. Mass spectrometry yielded several results on photoionisation in the gas phase (F. I. Vilesov).

Two-quantum reactions involving triplet states of organic molecules form a special class of photochemical processes. Kh. S. Bagdasar'yan examined the kinetics of the sensitised dehydrogenation of alcohols, which has a two-quantum mechanism, and made the first measurements of the absolute efficiencies of the two-quantum photoionisation of organic compounds in a condensed phase. N. V. Fok, M. V. Alfimov, V. E. Kholmogorov also investigated two-quantum processes.

The discovery and manufacture of laser sources of radiation led to promising new lines of research in photochemistry. It was established that infrared rays were photochemically active, ensuring the selective occurrence of a reaction whose activation energy was substantially larger than the energy of an infrared quantum (N. G. Basov, A. N. Oraevskii, A. V. Pankratov).

The development of modern pulse methods has permitted the study of extraordinarily fast photoprocesses (down to

10^{-9} s), which is of fundamental importance for investigation of the mechanism of elementary reactions. A flash fluorometer has been used to study heterolytic dissociation and the phototransfer of an electron and a proton (M. G. Kuz'min). A kinetic study has been made of the protonation of excited acridine molecules (Fig. 18). In the course of an investigation of intermediate products in the flash photolysis of solutions of various phenols in the presence of compounds of transition metals (V. A. Kuz'min and I. V. Khudyakov) complex formation was established between the *o*-methylphenoxyl radical and cobalt acetylacetonate (Fig. 19).

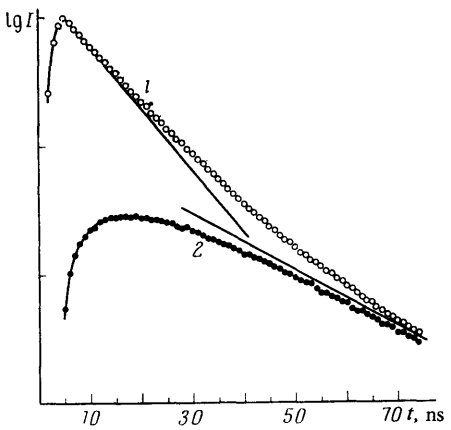


Figure 18. Kinetics of the fluorescence in aqueous solution of: 1) acridine; 2) the acridinium ion.

In order to prepare materials possessing superconducting and semiconducting properties, K. N. Anisimov and N. E. Kolobova investigated the photochemical reaction of tetracarbonyl-π-cyclopentadienylniobium with silicon, germanium, and tin acetylides.

Photosubstitution in aromatic compounds and the photoreduction of aromatic nitro-compounds have been investigated (A. V. El'tsov).

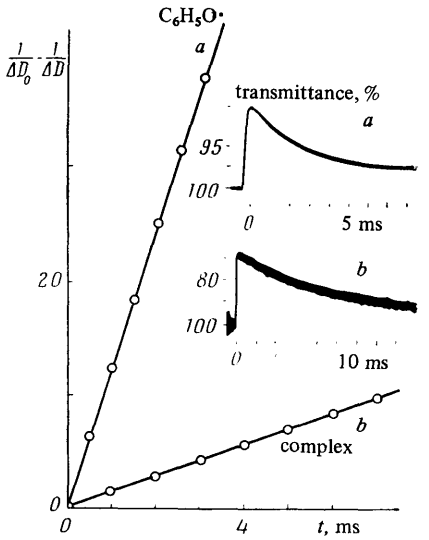


Figure 19. Kinetic curves of the decay of: *a*) *o*-methylphenoxyl radical; *b*) complex of *o*-methylphenoxyl radical with cobalt acetylacetonate.

The widespread application of photochromic compounds in technology led to an intense investigation of their properties and of the mechanism of photochromism (V. A. Krongauz, K. G. Dzhaparidze, M. A. Gal'bershtam). Work is being undertaken on the synthesis of new photochromic compounds based on spiropyrans, which absorb visible light (E. R. Zakhs, L. S. Efros).

One problem of present-day science and technology of photographic materials is to obtain emulsions that possess high sensitivity over a wide spectral range. I. I. Levkoev and A. I. Kiprianov prepared efficient new spectral sensitisers for various photographic materials, and introduced these polymethine dyes into industry.

K. V. Chibisov investigated the photochemistry of photographic processes. He discovered the nature of photographic sensitivity, and examined the mechanism of the chemical sensitisation of photographic emulsions.

Photochemical methods have proved effective in the chemistry and technology of polymers. Monolithic glasses of any thickness have been obtained by photopolymerisation for the first time on an industrial scale (S. R. Rafikov, G. P. Gladyshev).

An important sector is preparative organic photochemistry. V. F. Kucherov has studied the photoinduced *C*-addition of alcohols, acetals, ethers, and esters to acetylene and its monosubstituted derivatives. Alkene systems substituted by various functional groups have been obtained by means of this reaction.

S. Ya. Pshezhetskii examined the effect of the medium on the mechanism of the photoconversion of free radicals in solutions of ethers and anhydrides of monocarboxylic acids. The formation of hydrogen bonds between radicals and molecules in alcohols and acids plays an important part in such processes.

The modelling of various photobiological processes and the investigation of the photochemical reactions of biologically important molecules constitute an actively developing line of research. A. A. Krasnovskii and V. B. Evstigneev have made a series of studies of the redox photoreactions of chlorophyll and related compounds in various systems. Elementary photochemical processes involving photosynthetic pigments and other metal-containing porphyrin compounds have been investigated by A. K. Chibisov, G. P. Gurinovich, A. N. Sevchenko, K. N. Solov'ev, I. I. Dilung. Artificial photosynthetic systems are being examined by G. G. Komissarov.

Reversible photochemical changes undergone by the visual pigment rhodopsin are being investigated (M. A. Ostrovskii, V. A. Krongauz).

I. V. Berezin, K. Martinek, and N. F. Kazanskaya have proposed a new chemical system for intensifying a light signal by means of enzymic reactions. The high quantum yield (10^{10}–10^{12}) can be utilised for the production of new supersensitive materials.

Photoinduced free-radical processes involving proteins are being studied (L. P. Kayushin).

Electrochemistry

Although the first electrochemical investigations in Russia were made as early as the nineteenth century by V. V. Petrov, F. F. Grotgus, B. S. Yakobi, E. Kh. Lents, A. S. Savel'ev, A. P. Sokolov, only the applied aspects of this important branch of physical chemistry were largely developed right up to post-Revolutionary times. The Soviet period is characterised by intense activity on the problems of electrochemistry. Many investigations have been made on the structure of the electrical double layer, the effect of adsorption on the kinetics of electrode processes, the role of diffusion factors, the theory of hydrogen overpotential, the quantum-mechanical theory of electrode processes, the electrochemical theory of corrosion and passivity, the mechanism of metal electrodeposition, and the electrochemistry of melts.

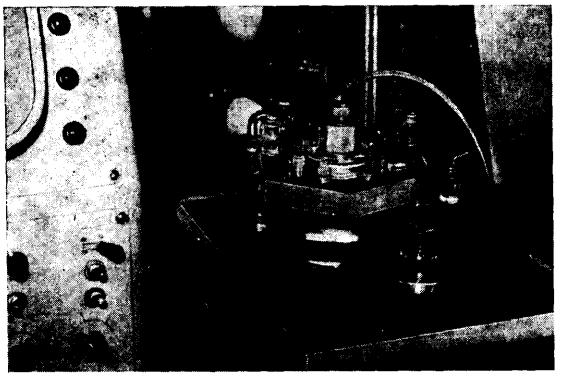


Figure 20. Apparatus for determining dependence of solid–liquid interfacial tension on surface charge (Institute of Electrochemistry of the USSR Academy of Sciences).

The most eminent electrochemical school in our country is that of A. N. Frumkin. As early as the 1930s he established the relation between the rate of reaction and the structure of the electrical double layer. The rate of discharge of ions was shown to be determined by their concentration at the electrode surface and to depend on the potential drop in the dense region of the double layer acting directly on the ions. Frumkin introduced the concept of the zero-charge potential as an individual characteristic of metals, which led to a solution of one of the problems of the theory of voltaic cells—the relation between their electromotive force and the contact potential difference between the two metals in a vacuum (the so called Volta problem). This work laid the foundations of quantitative electrochemical kinetics. Frumkin's school developed and perfected methods for investigating the metal—solution interface, measuring the capacitance of electrodes by means of alternating currents, determining charging curves and the adsorption of labelled atoms, and applying the isoelectric displacement method (P. I. Dolin, B. V. Ershler, N. A. Balashova, V. E. Kazarinov, O. A. Petrii). A quantitative theory of the double layer and a theory of adsorption at charged interfaces were elaborated (B. B. Damaskin).

During recent years advances have been made in the quantum-chemical interpretation and experimental investigation of the mechanism of the elementary step in electrode reactions and processes in the bulk solution which accompany electron transfer (R. R. Dogonadze, A. M. Kuznetsov, L. I. Krishtalik). A new electrochemical field—the electrochemistry of solvated electrons—was developed. Krishtalik has established the laws of dark emission, and A. M. Brodskii, Yu. V. Pleskov, et al. those of the photoemission of electrons from a metal into a solution. The theory of convective diffusion (V. G. Levich) helps to solve the problems of the transport of material to the electrode surface.

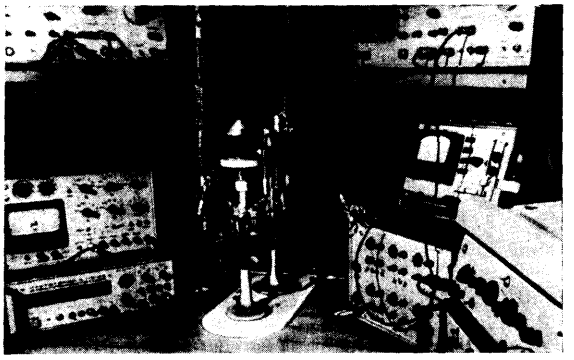


Figure 21. Apparatus for potentiometric investigation of state of surface and kinetics of electrochemical reactions using a rotating disc electrode with a ring (Institute of Electrochemistry of the USSR Academy of Sciences).

A. N. Frumkin and L. N. Nekrasov have proposed a disc electrode with a ring (Fig. 21) for investigating intermediate products of electrochemical processes.

A theory of the establishment of a potential on ion-selective membranes has appeared in papers by B. P. Nikol'skii, M. M. Shult's, and their coworkers; new types of glass and other ion-selective electrodes have also been developed.

The theory of corrosion processes and the struggle against corrosion have been widely researched, beginning with the investigations of V. A. Kistyakovskii and N. A. Izgaryshev. This work has been developed by G. V. Akimov, who put forward a theory of multicomponent systems containing metal–solution microsystems differing in structure and properties, and by Frumkin (the theory of coupled reactions). Ya. M. Kolotyrkin obtained important results on the theory of corrosion and on methods of corrosion protection. He revealed the role of complex formation and established experimentally for the first time the direct involvement of water molecules in the electrochemical stages of the dissolution of active metals (nickel, manganese). He showed that a purely chemical mechanism of dissolution of metals was possible in addition to the electrochemical mechanism. N. D. Tomashov suggested a novel method for producing corrosion-resistant alloys by cathodic alloying, i.e. by introducing into the alloy small quantities of such components as palladium, platinum, ruthenium, etc., which accelerate the cathodic evolution of hydrogen.

K. M. Gorbunova and P. D. Dankov studied the mechanism of crystal growth and nucleation during electrolysis; they worked out the theory and a technology of chemical nickel plating. Yu. Yu. Matulis is undertaking comprehensive investigations on the electrodeposition of metals and the production of the bright coatings used in industry. G. S. Vozdvizhenskii has studied the electrolytic polishing of metals.

The Ural school has made a great contribution to the development of high-temperature electrochemistry. Data have been obtained on electrochemical kinetics in molten salts and on the structure of the electrical double layer at the boundary between molten metals and electrolytes (S. V. Karpachev, O. A. Esin, M. V. Smirnov, V. A. Kuznetsov, E. A. Ukshe). Diffusion kinetics in molten salts has been investigated by Yu. K. Delimarskii. The possibility has been established of using solid electrodes for polarographic purposes and of applying polarography to the study of complex formation in melts.

The development of fuel cells—devices in which the chemical energy of the fuel is converted directly into electrical energy—has stimulated a number of theoretical investigations. The mechanism of processes occurring in fuel cells (the ionisation of hydrogen and the electrochemical reduction of oxygen) has been examined, the phenomena of electrocatalysis have been studied, model systems have been analysed, and a theory of mass transfer in porous electrodes has been developed which permits more efficient utilisation of their surface (V. S. Bagotskii, A. G. Pshenichnikov, R. Kh. Burshtein). Most of the work in this field has been undertaken by industrial institutes. The experience accumulated in work on the hydrogen—oxygen fuel cell has been used to lower the voltage in the electrolysis of water. The development of high-temperature fuel cells has led to a theory of conduction by solid electrolytes in equilibrium with the gas phase (S. F. Pal'guev).

The Institute of Electrochemistry of the USSR Academy of Sciences has recently developed electrochemical transformers (memory cells, integrators, pressure and acceleration transducers, etc.), which materially supplement semiconductor devices at low frequencies and in control by weak signals (P. D. Dukovtsev, B. M. Grafov).

Chemical Thermodynamics

The foundations of thermochemistry as a science were laid by the work of G. I. Gess [Hess]. The law which he discovered, that the total heat of a chemical reaction is independent of the intermediate states of the system, is a particular formulation of the first law of thermodynamics. Systematic and accurate thermochemical investigations have been made by B. F. Luginin, M. M. Popov, S. M. Skuratov, and others.

Generalisation and systematisation of experimental thermochemical results led to the discovery of several regularities. D. P. Konovalov (1924) proposed the well known relation for determining heats of combustion of organic compounds from their composition and their membership of a known homologous series. A. M. Berkengeim (1925) established that heats of formation of inorganic compounds can be calculated as the arithmetic means of the values for the corresponding compounds of the adjacent elements (in a series or a group of the Periodic System). A. F. Kapustinskii showed that the heats of formation of many crystalline compounds of the same type vary linearly with the logarithm of the atomic number of the elements, and suggested a formula for calculating the entropies of ions (in crystal lattices) from the atomic weights of the elements, their valencies, and the ionic radii. V. A. Kireev demonstrated the existence of a simple approximation enabling entropies of formation of crystalline compounds to be computed from their composition.

N. N. Beketov's studies of the reversibility of chemical processes—the dependence of the direction of chemical changes in a system on the concentrations (pressures) of the reactants—played an important part in the development of chemical thermodynamics. This work led to the discovery of the law of mass action—a thermodynamic relation of the greatest importance for chemistry.

Equations of state of gases play a large part in thermodynamics. The Mendeleev–Clapeyron equation of state of ideal gases is widely used. New lines of investigation appeared in the post-Revolutionary period. A general theory of thermodynamic potentials was based by S. A. Boguslavskii on statistical mechanics. The fundamental concepts of thermodynamics have been refined and its theory has been presented more rigorously, the irreversibility of processes has been studied, and the second law of thermodynamics has been analysed (G. A. Afanas'eva-Erenfest, K. A. Putilov), geometrical thermodynamics has been developed (A. B. Mlodzievskii), the thermodynamics of intermolecular interaction investigated (E. S. Rudakov), the thermodynamics of irreversible processes developed (A. I. Veinik), and interaction in multicomponent systems with a variable number of degrees of freedom examined (L. S. Palatnik, A. I. Landau). The requirements of technology for numerical thermodynamic characteristics with wide variation in physical conditions stimulated experimental lines of attack on thermodynamics and promoted the development of methods for the statistical calculation of thermodynamic data. Ya. B. Zel'dovich, A. N. Gurvich, and Yu. M. Shaulov worked out methods for the thermodynamic calculation of combustion processes and explosions. Systematic statistical calculations of thermodynamic data at high temperatures were made by A. V. Frost and I. N. Godnev.

Study of the thermodynamic properties of individual groups of substances used in the new technology (new fuels, semiconducting materials, compounds of rare metals, strong alloys, durable coatings, etc.) is most important for the national economy of the USSR. Ya. I. Gerasimov has devoted his efforts to an important branch of experimental thermodynamics—determination of the free energies of compounds used in non-ferrous metallurgy and the study of heat-resistant alloys, oxides, and semiconductors.

M. Kh. Karapet'yants has elaborated a set of methods for the comparative calculation of several physicochemical properties of various chemical compounds.

Among theoretical investigations mention must be made of the work of L. D. Landau and V. K. Semenchenko on phase transitions of the second kind and on the theory of the thermodynamic stability of systems. D. S. Korzhinskii has applied to geological processes the concept of heterogeneous equilibria in open multiphase and multicomponent systems.

Thermodynamic functions for individual inorganic compounds, groups of compounds, solutions, and alloys have been investigated by many workers in connection with theoretical generalisations and practical problems (E. V. Britske, G. V. Kurdyumov, A. F. Kapustinskii, V. A. Sokolov, N. K. Voskresenskaya, A. I. Vol'skii, A. A. Zhukhovitskii, K. P. Mishchenko, M. M. Popov, K. G. Khomyakov, A. V. Rakovskii, S. M. Skuratov, A. M. Samarin, N. V. Ageev, S. A. Shchukarev).

Liquids and Solutions

Study of the properties of pure liquids and solutions is closely related both to thermodynamics and to aspects of the theory of the structure of matter. However, thermodynamic methods for describing the properties of solutions are the most important at present, because of inadequate development of a molecular—statistical theory of liquids.

The first systematic investigations of the miscibility of liquids were made by V. F. Alekseev during 1878–1884, and played an important role in establishing a thermodynamic theory of solutions. Alekseev also enunciated the "law of the rectilinear diameters" used to estimate the parameters of the critical points of two-phase systems. He visualised dissolution as resulting from two opposing tendencies—thermal motion of the molecules and "chemical" intermolecular interaction. In his general views he was an adherent rather of the physical theory of solutions, although he acknowledged its limited character.

D. I. Mendeleev was one of the authors of the "chemical" theory of solutions. He recognised the role of "physical" factors, but did not regard them as uniquely important in the theory of solutions, especially for solutions of finite concentration. The correctness of this general view has already been quite definitely confirmed in the unification of the general ideas and methods of the physical and chemical theories. In this connection an important role was played by the views of I. A. Kablukov, who regarded solvation as the main cause of the formation of ions in solution.

D. P. Konovalov worked on the thermodynamics of solutions. His study of the vapour pressure of various binary mixtures was crowned by the formulation of his well known laws. Konovalov's laws on the one hand provided a basis for a systematic thermodynamic analysis of the properties of solutions, and on the other hand are widely used in the practical rectification of liquids and in the theory of the distillation of liquid mixtures.

D. K. Chernov made the first investigations on solid solutions and phase diagrams. His "critical points", which have an important role in practical ferrous metallurgy, are actually transition temperatures of solid phases in the iron–carbon system.

Gaseous solutions have been studied. I. R. Krichevskii, P. E. Bol'shakov, and D. S. Tsiklis discovered the limited miscibility of gases in the case of the ammonia–nitrogen system. Similar properties have since been observed in several other systems.

N. S. Kurnakov's investigations on phase equilibria in solution are closely related to the theory of solutions. They led to the foundation of physicochemical analysis on the principles of continuity and congruence, later supplemented by the concept of singular points on phase diagrams. Physicochemical analysis not only was a method for the general description of phase diagrams but also acquired great practical value in the exploitation of salt deposits in the USSR.

Ya. I. Frenkel' was the first to attempt a consistent phenomenological theory of the liquid state based on the special character of molecular motion in a liquid. The movement of a given molecule is determined by the molecular field due to its environment and by its own kinetic energy. This motion is intermittent and is governed by the mean lifetime in temporary equilibrium positions. These ideas served as a basis for much subsequent work.

A more rigorous statistical theory of liquids and solutions, using the concept of correlative distribution functions of groups of particles, was elaborated by N. N. Bogolyubov. A statistically consistent method of calculating the thermodynamic properties of solutions of strong electrolytes, based on the method of correlation functions and variational derivatives, is widely used for solving stochastic problems. This method was developed further by I. Z. Fisher, who applied it in particular to solving the problem of the structure of liquids.

S. A. Shchukarev investigated the periodicity of the properties of chemical compounds in solutions, as well as aspects of chemical hydrology.

Thermodynamic methods of describing binary and multicomponent systems, by means of which possible types of phase equilibrium curves were established in heterogeneous multicomponent systems, were examined by A. V. Storonkin. A series of investigations of phase transitions in solutions of non-electrolytes at high pressures provided a better understanding of the relation between intermolecular interactions and thermodynamic properties (Krichevskii). Thermodynamic methods of calculating phase equilibria in liquid binary and multicomponent systems were evolved by V. B. Kogan for processes of azeotropic and extractive fractionation, from which technical schemes for the separation of mixtures were worked out. V. A. Mikhailov worked on thermodynamic processes of extraction. He suggested an extraction method for determining activity coefficients of electrolytes in aqueous solution.

V. K. Semenchenko demonstrated the effect of ion-pairs on the properties of electrolyte solutions, showed the physical pattern of this phenomenon, and gave its mathematical description. He introduced the concept of the generalised moment as a parameter representing a force constant (charge, dipole and quadrupole moments) per unit dimensions of the molecule. He based a general classification of solutions on a survey of the effective forces of interaction between particles. M. I. Shakhparonov investigated the structure of liquid systems with hydrogen bonds and thermal motion of the molecules.

A. I. Brodskii carried out series of experimental and theoretical investigations on strong electrolytes in non-aqueous media. A. N. Frumkin examined liquid solutions in terms of the energetics of solvation. K. B. Yatsimirskii considered regularities in the energies of formation of ions, together with aspects of proton affinity and ionic hydration.

The only quantitative theory of the dissociation of electrolytes and the theoretical principles of acid—base titration in non-aqueous media are due to N. A. Izmailov. Heats of dissolution in aqueous solutions of electrolytes (in contrast to non-aqueous solutions) become more strongly exothermic with rise in temperature, which indicates that the specific structure of water is a decisive factor in the energetics of the solutions. The idea of a limit of complete solvation has proved extremely useful in the discussion of salting out, acid catalysis, oxygen exchange between anions and water, and many other phenomena (A. M. Sukhotin, K. P. Mishchenko). The effect of the structure of water on the properties of solutions and its variation under the influence of ions have been examined by O. Ya. Samoilov.

Nuclear magnetic resonance, electron spin resonance, and non-resonant paramagnetic absorption have recently found wide application for investigating the structure of liquid solutions. A. I. Rivkind established that the relaxation of protons in solutions of paramagnetic salts takes place mainly in the solvation spheres of the paramagnetic particles, not in the bulk of the free solvent. Study of the relaxation of the solvent nuclei can be used as a method for examining the structure of paramagnetic solutions.

Magnetic resonance has been used to investigate the mobility of water molecules in the vicinity of ions and has confirmed the negative hydration of iodide and bromide ions. Negative and positive hydration of ions has been confirmed also by determining the translational diffusion coefficients of water in electrolyte solutions by the spin echo method (K. A. Valiev).

V. I. Danilov has used X-ray diffraction to investigate liquids and solutions. Analysis of the curves for scattering intensity reveals that liquids near the melting points are characterised by short-range order of the particles resembling their arrangement in the corresponding crystals.

Adsorption and Chromatography

The first work in Russia on adsorption was done as early as in 1785 by T. E. Lovits, who studied the adsorption of dyes on activated charcoal. Fundamental investigations on the adsorption of gases were made at the end of the nineteenth century and the beginning of the twentieth century. Classic studies in this field are those by A. A. Titov on the adsorption of gases on activated carbon and by N. A. Shilov on the dynamics of such adsorption.

During the First World War N. D. Zelinskii used the adsorptive power of carbon to produce a gas mask. The analytical possibilities of adsorption phenomena, and methods for separating mixtures based on differences in the adsorption of the components, were realised in 1903 by M. S. Tsvet. This worker used adsorbents to separate dyes and termed his method "chromatography". This method has found wide practical application only in our times, some fifty years after its creation.

The scope of work on adsorption became especially wide after the Bolshevik Revolution. Shilov and his pupils (S. A. Voskresenskii, L. K. Lepin', A. P. Ivanitskii, I. A. Tserevitinov) investigated the adsorption of solutes on carbon, and revealed the characteristic features of the adsorption of non-electrolytes and strong and weak electrolytes.

Soviet scientists have conducted a long series of investigations on the theory of adsorption phenomena. B. V. Il'in studied the role of intermolecular interactions in adsorption. A. N. Frumkin was the first to obtain an equation to the adsorption isotherm allowing for the mutual attraction of the molecules in the adsorbed layer. This equation was subsequently confirmed by more rigorous molecular–statistical calculation.

M. M. Dubinin evolved a theory that the space in pores became filled during adsorption, which enabled the adsorption isotherms of various vapours to be calculated from the known affinity coefficient and a characteristic curve obtained from the adsorption isotherm of one substance. Together with L. V. Radushkevich he established a relation between the form of the characteristic curve and the porosity of the carbon. The same methods have recently been used to study adsorption on zeolites. Methods have been worked out for obtaining many adsorbents of specified porosity. Dubinin's work on the dynamics of sorption gave rise to the chromatography of vapour mixtures.

A. V. Kiselev studied the adsorption of various classes of compounds on modified and unmodified silica gels, zeolites, and graphitised carbon black. Methods of adsorption, gas chromatography, and molecular spectroscopy were used in this work to investigate intermolecular interactions in general. Views were evolved on specific and non-specific adsorption, with the use of spectroscopy to study the former. Molecular–statistical calculations were employed to compute the main adsorption and gas-chromatographic characteristics of several hydrocarbons and other compounds on graphitised carbon black and on zeolites. A relation was found between the energy of adsorption and the properties of the sorbable molecules. Not only heats of adsorption but also heat capacities of various compounds in adsorbed layers were determined. The improvement of gas-chromatographic methods enabled hundreds of adsorbate–adsorbent systems to be investigated for extremely complicated organic and organoelementary compounds. Molecular liquid chromatography and adsorption from solutions were used to study the intermolecular interactions of simple organic molecules, polymers, biopolymers, and viruses.

In connection with the study of catalytic processes many theoretical and experimental investigations were made on the chemisorption of active gases on energetically non-uniform surfaces. The logarithmic adsorption isotherm first found experimentally (A. I. Shlygin, A. N. Frumkin) was explained theoretically both by the concept of energetic non-uniformity (L. D. Landau, Ya. B. Zel'dovich, S. Z. Roginskii) and by the action of intermolecular forces of repulsion (M. I. Temkin). Zel'dovich was able to show how the distribution function of heats of adsorption could be determined from the experimental equation for the adsorption isotherm, which gave rise to a long series of studies in this field (Roginskii, Temkin).

V. K. Semenchenko studied adsorption phenomena in metallic systems, and discovered several specific effects attributable to the high surface activity of individual components of the alloy. The effect of surface-active metals on the brittleness of metals and alloys was discovered by P. A. Rebinder, Yu. V. Goryunov, and E. D. Shchukin ("Rebinder effect").

K. V. Chmutov is investigating the separation of rare-earth metals, the role of complex formation, and the simulation and intensification of chromatographic processes. V. A. Malyusov has been concerned with the theoretical principles of separation processes (chromatography, fractionation, crystallisation).

G. M. Panchenkov is concerned with ion-exchange equilibria on zeolites and the thermodynamics of heterogeneous equilibria. A. A. Zhukhovitskii has used the theory of mass transfer to describe the dynamics of sorption. The principles of mass transfer and the problems of the automation and optimisation of chemical processes are being dealt with by V. V. Kafarov. Sorption in a fluidised bed has been investigated by D. G. Romankov, who has generalised the equations of sorption dynamics.

The work of E. V. Alekseevskii and his students is widely known in the field of non-carbon adsorbents. They have developed methods for the preparation of active metal oxides and have studied the recovery of various solvents. I. V. Grebenshchikov discovered siliceous adsorbents having a spongy structure–porous glasses.

The laws of the sorption of ions by activated charcoals and silica gels, the mechanism of the adsorption of various complex compounds, and the role of electrochemical factors in these phenomena were studied by D. N. Strazhesko and his coworkers.

Colloid Chemistry

Colloid chemistry began to develop as a physicochemical discipline in the second half of the nineteenth century.

Before that time, however, there were investigations which played a significant role in the establishment of colloid chemistry and its methods. These include the discovery of electrokinetic phenomena—electrophoresis and electro-osmosis (F. F. Reiss)—the first quantitative studies of the formation of jellies and gels (F. N. Shvedov), cryoscopic measurements of the effective molecular weights of various substances in colloidal solution (N. N. Lyubavin, A. N. Sabaneev), and work on the theory of capillarity (A. Yu. Davidov, I. S. Gromeka).

Modern ideas on the nature and properties of the colloidal state are due to P. A. Rebinder and his school (A. B. Taubman, V. I. Likhtman, E. D. Shchukin, et al.). Several fundamental principles of the physical chemistry of surface phenomena in disperse systems were established (evolution and stability of structures, control of their properties by the introduction of surface-active agents). These investigations provided a scientific basis for the application of flotation agents, stabilisers, detergents, demulsifiers, etc.

A. V. Dumanskii has revealed the role of complex formation in the production of colloidal particles, and of the bonding of water in the drying and denaturation of colloids. N. P. Peskov has examined the role of kinetics and state of aggregation in the stability of colloids as functions of their degree of dispersion and their kinetic and adsorption properties. Specific features of adsorption on swollen colloids have been studied by A. V. Rakovskii.

B. V. Deryagin investigated surface phenomena in terms of the action of surface forces. A quantitative theory of the coagulation of disperse systems by electrolytes was formulated that took into account the relative molecular attraction. Direct measurement of the forces acting between surfaces at distances of the order of a micrometre provided experimental verification of the present-day physical theory of long-range molecular action. Cross-linked colloidal systems have been investigated by M. P. Volarovich, A. A. Trapeznikov, K. F. Zhigach, G. V. Vinogradov, and others.

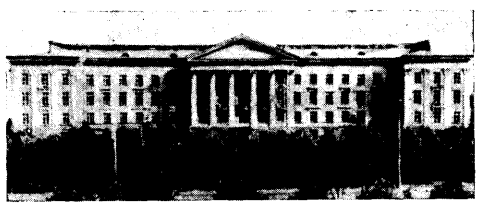


Figure 22. Zelinskii Institute of Organic Chemistry of the USSR Academy of Sciences.

Electrochemical methods are widely used in the study of colloids (A. I. Rabinovich, V. A. Kargin, N. I. Zhukov, and others). An effective method for purifying colloidal systems by high-voltage electrodialysis has been developed from this work. Electron microscopy has revealed the mechanism of the formation of colloidal particles.

The properties of solutions of polymers and the aging and syneresis of jellies have been investigated by S. M. Lipatov and S. A. Glikman. The colloidal properties of proteins were studied by A. G. Pasynskii, V. A. Pchelin.

Numerous applications of aerodisperse systems have been examined. An effective procedure for preventing the formation by radiation of mists of water droplets, based on blocking the hygroscopic condensation centres by adsorbed monolayers of higher alcohols, has been evaluated (B. V. Deryagin, P. S. Prokhorov, V. A. Fedoseev, N. N. Tunitskii, Ya. I. Kagan, A. G. Amelin, I. V. Petryanov-Sokolov).

Work has progressed on applications of colloid chemistry to the food industry (A. V. Dumanskii, N. F. Ermolenko) the rubber and synthetic rubber industry (B. A. Dogadkin, S. S. Voyutskii, A. I. Yurzhenko), dyes (N. P. Peskov, L. I. Belen'kii), cellulose (S. M. Lipatov), etc.

Trapeznikov has developed methods and apparatus for investigating the rheology of cross-linked systems and the mechanical properties of monolayers and soap films.

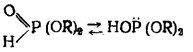
ORGANIC CHEMISTRY

Research on organic chemistry became widespread after the middle of the past century. Fundamental work was done by A. M. Butlerov—author of the theory of the structure of organic compounds—A. E. Favorskii, S. V. Lebedev, N. N. Zinin, N. D. Zelinskii, V. V. Markovnikov. The first institute of the Academy of Sciences to specialise in research on organic compounds was established at Moscow in 1934, and is now the Zelinskii Institute of Organic Chemistry [Fig. 22].

Modern organic chemistry, which already deals with millions of compounds, has been transformed, in the words of A. N. Nesmeyanov, into the structural architecture of molecules.

Theoretical Foundations of Organic Chemistry

A. M. Butlerov's theory of the chemical structure of organic compounds blazed a trail, in the "dense forest" (Wöhler's expression) of organic chemistry, to an understanding of the nature of quadrivalent carbon compounds. Butlerov noted the decisive importance of the interaction of atoms and groups in the molecule, explained the isomerism of the hydrocarbon residues, and was the first to direct attention to the possibility of isomeric conversion (cyanic acid, urea). In 1877 Butlerov pointed out that isodibutylene [2,4,4-trimethylpent-2-ene] was able to react according to two structural formulae or, in the modern idiom, it had dual reactivity. This was the first example of equilibrium isomerism (tautomerism), an understanding of which has been greatly assisted by the work of A. E. Favorskii and A. E. Porai-Koshits. Milestones on the road to a theory of tautomerism and dual reactivity were the discovery of a new type of dyad tautomerism in dialkyl phosphites (A. E. Arbuzov)



and investigation of the reactions of the tautomeric 2-aminopyridine and methylpyridine systems (A. E. Chichibabin). The concept of intramolecular valency tautomerism was first applied in dye chemistry.

Investigations showing the possibility of dual reactivity in the absence of tautomerism constituted a definite stage of development in theoretical organic chemistry. A. N. Nesmeyanov and M. I. Kabachnik drew a sharp distinction between equilibrium dynamic isomerism (tautomerism) and dual reactivity, and worked out a strict classification of various cases of the latter with and without migration of the reaction centre along the chain of conjugated

bonds. The influence of various factors was considered, and quantitative relations were established between the kinetic parameters of the reactions and the solvent, the temperature, and the nature of the reactants. Several general rules were formulated, the application of correlation equations was worked out, and new methods were found for investigating diverse tautomeric systems. It was shown that, in cases of strongly displaced equilibrium, the reaction product corresponding to the tautomer present in low concentration is formed from the other tautomer with transference of the reaction centre. The factors determining the conditions of such transfer have been examined.

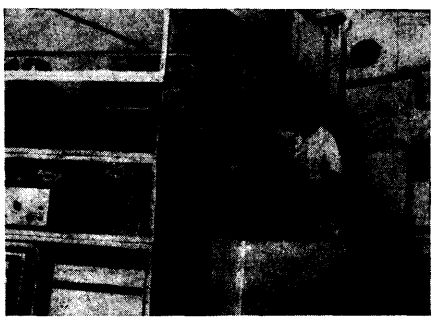
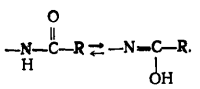
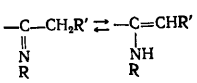


Figure 23. Radiation installation for investigating the mechanism of catalytic reactions during exposure to γ-rays (Institute of Organic Chemistry of the USSR Academy of Sciences).

The tautomerism of many nitrogen-containing heterocyclic systems have been studied by infrared and ultraviolet spectroscopy, and the conditions of displacement of the tautomeric equilibrium have been revealed as functions of the nature of the substituent and the solvent (I. Ya. Postovskii, Yu. N. Sheinker, I. I. Grandberg). The structure of tautomeric and potentially tautomeric nitrogen-containing open-chain systems has been investigated. Thus the application of spectropolarimetry to optically active compounds has revealed amide–imidol tautomerism



It has been used to investigate the tautomeric equilibrium of the ketimide–enamine system



(V. M. Potapov, A. P. Terent'ev), previously detected from the infrared spectra (N. K. Kochetkov, Ya. V. Dombrovskii). M. M. Shemyakin discovered a variety of ring–chain tautomerism involving the amide group, and proposed an isotope method for discriminating between tautomerism and dual reactivity. This method was able to record, for example, the high rate of tautomerisation of diazoaminobenzene, which explains the specific behaviour of the triazen system.

S. S. Novikov published a series of papers on the tautomerism, structure, kinetics, and reaction mechanism of nitroalkanes and their salts. To elucidate the nature of keto–enol tautomerism use has been made of infrared and Raman spectroscopy (D. N. Shigorin, V. A. Mironov, Yu. A. Pentin), as well as high-resolution proton magnetic resonance spectroscopy (E. I. Fedin).

New types of tautomerism—metallotropy, acylotropy, and aroylotropy—have been discovered and studied in several organophosphorus compounds.

The investigation of *O*- and *C*-hetero-substituted derivatives of monocarbonyl and β-dicarbonyl compounds has revealed many examples of dual reactivity. Isomerisation has been observed with migration of the heteroatom (silicon, phosphorus, arsenic, etc.) from carbon to oxygen and from oxygen to carbon in the keto-enol. Heterotropic tautomerisations have been studied in acetone derivatives containing germanium, tin, and antimony (I. F. Lutsenko). It has thus been shown that the well known prototropic tautomeric equilibria represent a particular—though evidently most important—case of the general phenomenon of heterotropic equilibria.

The study of molecular rearrangements is of great value for understanding reaction mechanisms and in the search for paths for the controlled synthesis of compounds of definite structure. Various conversions resulting from molecular rearrangements have been investigated by E. E. Vagner, S. S. Nametkin, A. E. Arbuzov, A. E. Favorskii, N. Ya. Dem'yanov.

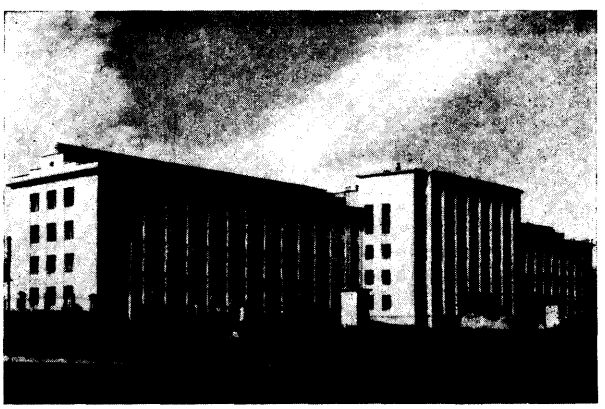


Figure 24. Arbuzov Institute of Organic and Physical Chemistry of the USSR Academy of Sciences.

B. A. Kazanskii's conversion of isopropenylcyclobutane into 1,2- and 3,3-dimethylcyclopentenes was an interesting example of the Vagner–Nametkin rearrangement. I. N. Nazarov extended the concepts of the Favorskii rearrangement to secondary and tertiary polyene alcohols. V. F. Kucherov and M. I. Ushakov discovered the rearrangement of furan derivatives involving multiple bonds. T. A. Favorskaya has found acetylene—allene and allene–diene rearrangements with acetylenic carbinols and halides. The reverse isomerisation (allene–acetylene) was described by A. A. Petrov. Favorskii's mechanism of the acyloin rearrangement of α-hydroxy-ketones was confirmed

by T. I. Temnikova. The rearrangement of α-hydroxy-aldehydes into hydroxy-ketones and α-glycols was studied by S. N. Danilov and E. D. Venus-Danilova. A mechanism was suggested for the aldehyde–ketone rearrangement by T. E. Zalesskaya. The Dem'yanov rearrangement was developed by N. I. Putokhin for the interconversion of five- and six-membered heterocycles. I. L. Knunyants found that polyfluorinated azides underwent a peculiar rearrangement into hydroxamic acids.

A. N. Nesmeyanov and R. Kh. Freidlina studied many examples of the rearrangement of radicals with 1,2-migration of chlorine and thiyl groups. The telomerisation and rearrangements of radicals in the reaction of ethylene with carboxylic acids and their derivatives were investigated, and used to develop an industrial method of producing α-branched monocarboxylic acids. The chemical behaviour of free radicals in the liquid phase was examined by G. A. Razuvaev. A study was made of chain reactions initiated by free radicals generated by irradiation or by the thermal decomposition of organometallic compounds.

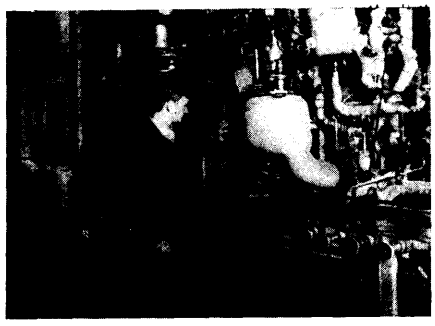
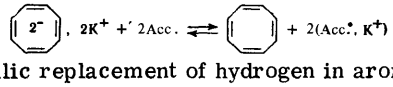


Figure 25. In the Technological Laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences.

The mechanisms of various organic reactions are being investigated by modern physicochemical methods. A procedure has been worked out for studying electron-transfer reactions in homogeneous media. The cyclo-octatetraene dianion is used as electron-donor, and the extent of reaction is assessed from the yield of neutral cyclo-octatetraene:

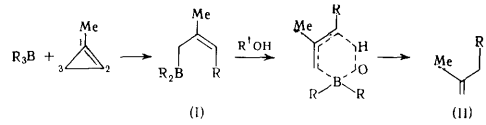


Nucleophilic replacement of hydrogen in aromatic compounds has been accomplished by abstraction of a hydride ion from anionic complexes. σ-Complexes of trinitrobenzene with acetone are oxidised by a wide range of oxidants—halogens, hypohalites, salts of metals of variable valency, peroxides, quinones, tropylium salts, etc.—to give high yields of trinitroacetone. Anionic σ-complexes of trinitrobenzene with compounds of transition metals have been obtained for the first time.

It has been suggested that double bonds can be selectively hydrogenated by silanes in acid solutions in the absence of a catalyst (ionic hydrogenation). The hydrogenation of thiophens under mild conditions gives high yields of the normally difficultly accessible thiophans, which are of great interest for their physiological (e.g. biotin) and antioxidant properties (D. N. Kursanov, Z. N. Parnes, V. N. Setkina, Z. V. Todres).

The mechanism of the oxidation of polymethylated aromatic compounds on reaction with electrophilic reagents in strongly acid media has been elucidated. The formation of intermediate species can be observed by proton magnetic resonance if the reactants are mixed at −80° to −100°C and the system is gradually "unfrozen". Voluminous information has been obtained on the mechanisms of these reactions, and convenient methods have been found for obtaining a series of compounds of practical interest (e.g. *p*-methoxytetramethylphenol and its derivatives, which have been tried as stabilisers for certain types of polymer systems (V. A. Koptyug)).

Investigation of the action of organoboranes on the highly strained cyclopropene system showed that 1-methylcyclopropene reacts with trialkylboranes under mild conditions with cleavage of the cyclic $C_{(2)}-C_{(3)}$ single bond:



(I) (II)

The resulting boranes of type (I) react with alcohols to give (after allylic rearrangement) the alk-1-ene (II). Conducting this reaction in alcohol will give in a single stage 60–90% yields of alkenes containing a terminal methylallyl group (B. A. Kazanskii, B. M. Mikhailov).

The mechanism of the spontaneous redox reaction of aldehydes in alkaline media (in Cannizzaro reaction) has been investigated. The kinetic data were analysed by means of the alkalinity function, which is a measure of the ability of the medium to ionise a molecule of a weak acid. This approach enabled M. I. Vinnik to establish the composition of the reactive complexes in the Cannizzaro reactions of *m*-nitrobenzaldehyde and *p*-methoxybenzaldehyde.

A systematic investigation is being made of the reactivity of complexes of transition metals with π- and σ-aromatic ligands in electrophilic and protophilic isotope exchanges of hydrogen (Kursanov).

The conformational state in solutions of simple model polyhalogenated alkanes, obtained by telomerisation and containing three- or four-spin molecular fragments, has been investigated. The complicated proton magnetic resonance spectra have been analysed by the use of double homonuclear and heteronuclear resonance, a computer, and the preparation of deuterated analogues. Methods that have been developed for evaluating the conformational composition and the fine structure of chiral molecules are required to solve stereochemical problems of the telomerisation stages—addition and substitution involving aliphatic radicals.

A. N. Nesmeyanov and A. E. Borisov investigated substitution at an alkene carbon atom in 2-chlorovinyl derivatives of various metals, and formulated the rule that geometrical configuration is conserved during substitution at an olefinic carbon. O. A. Reutov and I. P. Beletskaya studied the kinetics, mechanism, and stereochemistry of substitution at a saturated carbon atom. Their investigations led to the well known rule that configuration is preserved in S_E2 reactions.

The dissociative resonance capture of electrons by molecules of various types of organic compound has been investigated by the mass spectrometry of negative ions (S. R. Rafikov, V. I. Khvostenko, R. G. Kostyanovskii).

Many investigations have involved the use of correlation equations, a method which has been widely accepted in the study of reactivity and reaction mechanisms (V. A. Pal'm, Yu. A. Zhdanov, V. I. Minkin).

Quantum-chemical methods have been used to calculate the geometry and the electronic state of organic molecules. This work began with Ya. K. Syrkin and M. E. Dyatkina's application of the Hückel method to the properties of organic compounds having conjugated bonds. A. A. Bochvar calculated the properties of organic molecules with alternating bond lengths. A. B. Bolotin and Yu. A. Kruglyak started the use of rapid electronic computers for molecular calculations. Programs were set up for evaluating molecular integrals (Bolotin). An original density matrix method was elaborated, and successfully applied to the calculation of certain physical properties of conjugated organic compounds (M. M. Mestechkin). A consistent theory was worked out for the interaction of electrons in conjugated systems, and their spectroscopic properties were explained (A. A. Ovchinnikov). A model was suggested for the elementary act of substitution in certain simple hydrocarbons (M. V. Bazilevskii).

Chemistry of Hydrocarbons

A systematic study of the structure and properties of hydrocarbons dates from the mid-nineteenth century, when many investigations were made by A. M. Butlerov and his school. The principles of the chemistry of petroleum hydrocarbons developed in the work of V. V. Markovnikov and N. D. Zelinskii, who were the first to direct attention to the importance of synthesising model compounds. The most reliable results will usually be obtained by comparing petroleum hydrocarbons with known standard (model) substances.

Methods for the synthesis of hydrocarbon standards were developed by B. A. Kazanskii, A. F. Plate, A. L. Liberman, who prepared various substituted cycloalkanes, isolated their geometric isomers, and synthesised several new bicyclic systems. R. Ya. Levina obtained previously unknown homologues of cyclohexane, isoalkanes, alkenes, alkynes, and compounds containing a tertiary carbon atom. V. N. Ipat'ev suggested methods for the preparation of alkenes from readily available oxygen-containing compounds, based on the example of the catalytic dehydration of alcohols. S. V. Lebedev converted ethanol into butadiene, and the mechanism of this reaction was studied by Yu. A. Gorin. The mode of preparation of isoprene from acetone and acetylene discovered by A. E. Favorskii formed the basis of V. F. Kucherov's method for the continuous synthesis of pure isoprene suitable for stereospecific polymerisation. At the beginning of the 1940s N. D. Zelinskii and A. L. Klebanskii accomplished the synthesis of butenyne and later hexa-1,5-dien-3-yne and its homologues.

At the beginning of the present century Ipat'ev and Zelinskii found ways of interconverting hydrocarbons, and were the first to study the hydrogenation of the benzene ring in aromatic compounds. This discovery initiated the development of catalytic organic synthesis. Numerous catalysts, widely employed for the hydrogenation and dehydrogenation of organic compounds, were evolved, and their mode of action was studied (N. I. Shuikin, Kh. M. Minachev, A. V. Frost, L. Kh. Freidlin, D. V. Sokol'skii, Yu. S. Zal'kind, A. M. Rubinshtein, B. L. Moldavskii). The hydrogenation of substituted ethylenes on platinum and palladium catalysts, as well as the hydrogenation of conjugated, vinylacetylenic, and acetylenic hydrocarbons, was studied by S. V. Lebedev, G. G. Koblyanskii, and A. I. Yakubchik. The results of this work were generalised as "Lebedev's rules". The dependence of the rate and order of hydrogenation on the substituents and structure of the isomers and on the free energy of the reaction was investigated. During the 1920–1940s Zelinskii and his pupils carried out a series of studies of the catalytic dehydrogenation of hydrocarbons: they determined methods and conditions for the dehydrogenation of various cyclohexanes, the efficiency of diverse catalysts, and the mechanism and kinetics of the catalytic processes. The results formed the basis for A. A. Balandin's multiplet theory of catalysis. Zelinskii's catalysed dehydrogenation was transformed into the chief method for studying natural petroleum hydrocarbons and became the principal industrial method of obtaining aromatic hydrocarbons. N. D. Zelinskii and N. L. Glinka discovered the catalytic conversion of cyclohexene into cyclohexane and benzene. This reaction, termed "irreversible catalysis", became the subject of numerous investigations, during which it was found to be common to all unsaturated cyclic hydrocarbons.

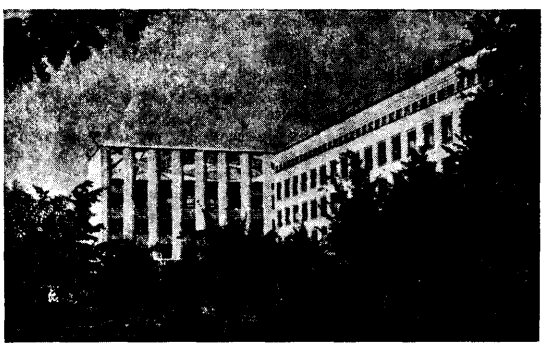


Figure 26. Institute of Organoelementary Compounds of the USSR Academy of Sciences.

Fresh results on the conversion of cyclohexane and cyclohexadiene on platinum and palladium have recently been obtained by V. M. Gryaznov and V. S. Smirnov, who show that the redistribution of hydrogen comprises a set of dehydrogenation and hydrogenation reactions. This discovery has been called membrane catalysis from the practical procedures adopted.

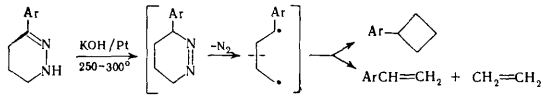
A simple transition from accessible alkanes to valuable aromatic hydrocarbons by means of dehydrogenating catalysts was achieved by three groups of investigators—B. L. Moldavskii and G. D. Kamusher, B. A. Kazanskii and A. F. Plate, and V. I. Karzhev—who studied various questions connected with the mechanism and the practical application of the dehydrogenation of alkanes. The hydrogenation of cyclopentanes—a new direct route to alkanes from the C_5 cycloalkanes widely distributed in petroleum—was discovered and studied, as well as isomeric changes in cyclic hydrocarbons.

Study of the alkylation of aromatic and aliphatic hydrocarbons, resulting from the need to synthesise high-octane components of motor fuel, was begun in the 1920s by

V. N. Ipat'ev, N. A. Orlov, and G. A. Razuvaev, after which it was developed simultaneously in many scientific establishments. Aspects of the synthesis of benzene homologues by means of various catalysts were considered by A. V. Topchiev, Yu. G. Mamedaliev, M. A. Dalin, Ya. M. Paushkin, and others. The catalytic alkylation of alkanes was studied in several investigations.

Work was done on the cracking of heavy petroleum products with the aim of obtaining motor fuel. Thermocatalytic conversions of individual hydrocarbons became one of the main subjects of investigation. M. G. Gonikberg, A. E. Gavrilova, and B. A. Kazanskii examined the effect of high pressure on the rate of thermal and catalytic cracking of alkanes. A. D. Stepukhovich suggested a reaction mechanism of cracking and a theory of the chain decomposition of alkanes. The kinetics, thermodynamics, and technology of the high-temperature processing of saturated hydrocarbon gases were studied systematically by A. M. Brodskii and K. P. Lavrovskii.

The chemistry of hydrocarbons having small rings is a comparatively young branch of organic chemistry. The publications of V. V. Markovnikov, G. G. Gustavson, N. D. Zelinskii, A. E. Favorskii, N. Ya. Dem'yanov, S. V. Lebedev, and N. M. Kizhner planned syntheses and described interesting isomerisations involving small rings, the mechanism of which has only now become clear. An explanation of the electronic structure of small rings was first given by M. E. Dyatkina and Ya. K. Syrkin. A series of studies on the mechanism of the formation of small rings from dibromides was made by Ya. M. Slobodin. Simple cyclic compounds and their isomerisation were investigated by Dem'yanov. The decomposition of pyrazolines, discovered by Kizhner, formed the basis for studies of various cyclopropanes (B. A. Kazanskii, M. Yu. Lukina, A. P. Meshcheryakov, L. V. Petrova). An interesting method of obtaining arylcyclobutanes was discovered in the 1960s by R. Ya. Levina, M. K. Kuz'min, Yu. S. Shabarov, who were studying the chemical and physical properties of arylcycloalkanes:



The stability of three- and four-membered rings was investigated (T. A. Favorskaya), as well as the dehydration and isomerisation of cycloalkylmethanols (Freidlin). The chemistry of small rings has been developed by I. A. D'yakonov, a pupil of Favorskii. This was one of the first researches on the use of carbenes for the synthesis of cyclopropane derivatives. A series of studies was made on the properties, mechanism of catalytic reactions, and spectral characteristics of three-membered rings with unsaturated and aryl substituents, together with the reactivity of cyclopropanes and halogenocyclopropanes.

The first investigations on the chemistry of acetylenic and conjugated systems were made by Favorskii and his students, who established methods of interconversion among acetylenes, allenes, and diene hydrocarbons, ways of passing from acetylenic compounds to terpenes, mechanisms of polymerisation, and various reactions of acetylenic hydrocarbons. This work opened up new fields of organic chemistry, in particular the chemistry of ethynylvinylmethanols (I. N. Nazarov, I. V. Torgov), butenyne (A. L. Klebanskii, A. A. Petrov, T. A. Favorskaya), and butadiyne (Yu. S. Zal'kind, A. D. Petrov, M. F. Shostakovskii). Research on the chemistry of acetylenic and conjugated compounds has immense value for the development of theoretical organic chemistry. Furthermore, these investigations have made available several new classes of unsaturated compounds which are important for the manufacture of synthetic materials.

The chemistry of terpene hydrocarbons has developed in our country by syntheses and studies of the structure and reactions of terpenes, investigations of the composition of native wood-chemical products such as essential oils, turpentines, and vegetable resins, as well as by industrial exploitation of the results. The chemistry of terpene hydrocarbons was studied by A. M. Butlerov, F. R. Vreden, F. M. Flavitskii, E. E. Vagner, L. A. Chugaev, and developed during the Soviet period by V. E. Tishchenko, A. E. Arbuzov, S. S. Nametkin, N. Ya. Dem'yanov, G. V. Pigulevskii, I. I. Bardyshev, V. N. Belov, V. I. Isagulyants, L. Ya. Bryusova, and many other investigators.

The oxidation, halogenation, and nitration of hydrocarbons were investigated because of the requirement by industrial developments to obtain valuable chemical raw material based on hydrocarbons of petroleum origin. The oxidation of organic compounds was studied by N. I. Chernozhukov, K. I. Ivanov, A. N. Bashkirov, V. V. Kamzolkin, V. K. Tsyskovskii, and many others. Researches on oxidising processes became especially interesting in connection with the study of their radical–chain mechanism, work which has been surveyed in the Physical Chemistry Section. Investigation of the halogenation of hydrocarbons was begun by V. V. Markovnikov and continued by A. V. Topchiev, B. A. Krentsel, N. I. Shuikin, who made many innovations both in the development of theoretical ideas in organic chemistry and in improving the technology of organic synthesis. Study of the nitration of hydrocarbons led to A. I. Titov's theoretical views, which are widely applied at the present time.

Aromatic and Heterocyclic Compounds

Aromatic compounds were already under investigation at the beginning of the nineteenth century. A. A. Voskresenskii discovered benzoquinone in 1838, and N. N. Zinin the reduction of aromatic nitro-compounds in 1842. Much work was done on the synthesis and various reactions of aromatic compounds (N. Ya. Dem'yanov, N. D. Zelinskii, N. M. Kizhner, A. E. Chichibabin, P. P. Alekseev, M. G. Kucherov), the nitration, chlorination, and sulphonation of benzene derivatives (N. N. Sokolov, F. F. Beil'shtein [Beilstein]), and the chemistry and technology of anthraquinone (M. A. Il'inskii).

Development of the chemistry of aromatic compounds during the Soviet period has promoted the establishment of a native industry of organic synthesis.

During the 1930s the mechanism of electrophilic substitution in the benzene ring was elucidated, and the dependence of sulphonation on various factors (concentration of sulphuric acid, temperature, presence of impurities) was determined (E. A. Shilov, V. A. Izmail'skii, A. M. Lukin, B. P. Fedorov, I. S. Ioffe). A kinetic study was made of the sulphonation of benzenes, the composition of the products was determined, and methods for the analysis of isomeric sulphonic acids were worked out (A. A. Spryskov). Study of the sulphonation of aromatic compounds occupied an important position in the work of N. N. Vorozhtsov, who investigated the sulphonation of naphthalene and the nature of its sulphonated derivatives, together with the effect of various catalysts on the reaction. Industrial methods were developed for the sulphonation of 2-naphthol (I. I. Vorontsov) and 2-chloronaphthalene (N. N. Vorozhtsov

Jr), as well as an effective method for sulphonating benzene in the vapour phase (R. K. Eikhman, M. I. Bogdanov, V. N. Ufimtsev).

The nitration of aromatic compounds began to be studied in the 1920s, when A. V. Kartashev detected the formation of nitrosophenols when phenol was treated with nitric acid. A. I. Titov carried out his classical work on the theory of nitration, and his suggested mechanisms and views on the nature of the nitrating agents became generally accepted. Many researches were devoted to a comprehensive study of the nitration of various aromatic molecules. The effect of boron trifluoride on the orientation of the nitro-group was determined, and a study made of the steric effect of nuclear substituents on the direction of reaction and the proportions of isomeric nitro-derivatives. Novel methods were worked out for obtaining aromatic nitro-compounds—by the batch and continuous nitration of ethylbenzene with a nitrating mixture, and simple methods for preparing *o*- and *p*-nitrobiphenyl, for obtaining chlorofluoronitrobenzenes, and for the simultaneous introduction of an iodine atom and a nitro-group into *p*-polyphenyl compounds. The nitration of anthraquinones, phenanthrene, acenaphthenes and fluorene, carbazole, dibenzopyrenes, and onium compounds has been investigated.

Vorozhtsov studied the effect of the nature of the catalyst on the kinetics of the chlorination of benzene, explained the mechanism of the catalytic action of iron(II) chloride, and worked out a continuous method of multiple chlorination. The kinetics and the mechanism of the halogenation of aromatic compounds in aqueous medium were examined by Shilov, who proposed an activity sequence of halogenating agents. He determined kinetic isotope effects in the halogenation of aromatic amines and amino- and hydroxy-sulphonic acids. The bromination of sterically hindered phenols was studied by V. V. Ershov and A. A. Volod'kin. The halogenation of more complex aromatic compounds—biphenyl, naphthalene, anthracene, anthraquinones, naphthacene, etc.—was investigated. Several new halogenating agents were suggested, e.g. *N*-chloroamides, *N*-chlorodiethylamine, *N*-bromophthalimide, and dioxan dibromide.

Considerable attention was paid to elucidating the mechanism of the alkylation of aromatic compounds in the presence of aluminium halides, in particular the chloride, whose first use in organic synthesis dates from G. G. Gustavson. The reactivity of alkylating agents towards aromatic hydrocarbons was studied, and schemes suitable for industrial use were proposed for the alkylation of benzenes by alkenes in the presence of aluminium chloride (N. N. Lebedev) and of sulphuric acid (Yu. G. Mamedaliev, M. A. Dalin).

During the 1920s V. M. Rodionov and V. K. Matveev discovered a new method for obtaining aromatic diazo-compounds from phenols and nitrous acid in a mineral medium, and this found industrial application. Azo-coupling, which with diazotisation is the principal reaction in the synthesis of azo-dyes, was studied in detail (A. E. Porai-Koshits).

Nucleophilic substitutions in the aromatic series were studied by A. N. Engel'gardt and P. A. Lachinov, N. N. Vorozhtsov Jr, D. V. Tishchenko, L. Kh. Freidlin, A. I. Kiprianov, E. Yu. Orlov, S. S. Gitis, B. I. Stepanov.

In the mid-1930s P. P. Shorygin and A. V. Topchiev began a systematic study of radical substitution in aromatic compounds. The mechanism and the chief laws of homolytic arylation were established by A. N. Nesmeyanov, Kh. S. Bagdasar'yan. Radical arylation by organometallic compounds was studied by G. A. Razuvaev. Many data on isomerisation in the aromatic series were summarised by V. A. Koptyug.

The chemistry of non-benzenoid aromatic systems has been vigorously developed during the past decades. Diphenylcyclopropenone, the cyclopentadienyl anion, cyclopentodienylides, and the tropylium and ditropylium cations have been investigated (D. N. Kursanov, M. E. Vol'pin, Yu. D. Koreshkov, Z. N. Parnes, I. S. Akhrem). Dipole moments have been measured (Ya. K. Syrkin, A. N. Shidlovskaya), and calculations made on the π-electron systems of certain compounds by the molecular orbital method (A. A. Bochvar).

The first investigations of heterocyclic compounds were made by Chichibabin, and their chemistry was developed by Rodionov's syntheses from β-amino-acids, A. I. Kiprianov and I. I. Levkoev's work on cyanine dyes, investigations of β-lactams and azalactones by I. L. Knunyants, studies by M. M. Shemyakin and V. K. Antonov on oxacyclic compounds, M. G. Voronkov on the chemistry of atran systems, B. A. Arbuzov on the diene synthesis of heterocyclic compounds, M. V. Rubtsov on azabicyclic compounds, and by many others. An original method of synthesising heterocyclic systems of diverse structure from substituted 2-chlorovinyl ketones was described by A. N. Nesmeyanov and N. K. Kochetkov. A general method for obtaining five-membered heterocycles from acetylenic α-oxides was worked out by F. Ya. Perveev.

A series of researches were made on furan derivatives. The reactions of chloromethylfurans, the preparation of nitrogen-containing heterocycles including a furan ring, diene synthesis and substitutive additions, and the reactivity of the furan ring were investigated by Yu. K. Yur'ev, K. Yu. Novitskii, N. S. Zefirov. Interconversion of five-membered heterocycles under conditions of vapour-phase catalysis by aluminium oxide was discovered to be a general reaction. Difficultly accessible 3-substituted furans were obtained, and Ya. L. Gol'dfarb elaborated a method for preparing ketones by acylating furan. A group of researches on the preparation, reactions, and practical application of furan derivatives is being conducted under the direction of S. A. Giller. Methods have been worked out for obtaining various functional derivatives of furan, and their pharmacological activity has been examined (A. L. Mndzhoyan). New methods for preparing furan derivatives —by sulphonation with pyridine—sulphur trioxide, formation of benzofurans from quinones, and production of amines of the furan series, whose oxidation yields amino-acids, some of which may be optically active—were proposed by A. P. Terent'ev. The hydrogenation and hydrogenolysis of furan compounds, as well as thermal and catalytic conversions of dihydrofurans, were studied by N. I. Shuikin.

New methods have been elaborated for the synthesis of pyrones, and their reactions have been studied (R. Ya. Levina, N. P. Shusherina, L. I. Zakharkin). Pyrylium salts, fused with a furan or a thiophen ring, have been investigated (G. N. Dorofeenko, Yu. A. Zhdanov).

The alkylation and acylation of thiophen in the presence of tin(IV) chloride has become generally accepted. A comparative study has been made of the direct metallation of the thiophen, furan, and benzene rings. A simple and effective method has been found for obtaining sulphides and thiols of the thiophen series, together with ways of preparing various functional derivatives.

Knunyants prepared propiothialactones, in which a new type of sulphur-containing four-membered ring has been formed. He also worked out original methods for alkylating 2-aminopyridine, as well as the principles for the industrial

production of quinacrine hydrochloride. N. N. Suvorov synthesised indol-3'-ylbutyric acid and found a new method of obtaining serotonin.

A. N. Kost investigated various nitrogen-containing heterocycles. Extensive investigations of diazaindenes and quinuclidines were made by L. N. Yakhontov in the search for physiologically active compounds. The chemistry of azines and azoles containing another heterocyclic atom (quinazolines, quinoxalines, phenoxazines, acridines, tetrazoles, benzimidazoles, etc.) is being investigated. New reactions non-activated heterocyclic substrates have been detected as well as the dealkylation of sterically hindered tertiary arylamines. The effects of a heterocycle and of other substituents on the amine–imine tautomerism and the conformation of formazans have been established (I. Ya. Postovskii).

Discovery of a new reaction of chlorinated aromatic and heterocyclic derivatives with hydrogen sulphide has been used to work out methods, suitable for industry, of obtaining aromatic and heterocyclic thiols and sulphides (M. G. Voronkov, A. S. Nakhmanovich, E. P. Deryagina). Aromatic and heterocyclic compounds and their fluorinated derivatives react with polyfluoroalkenes to give polyfluorobenzocycloalkenes (V. P. Mamaev).

The investigations of various classes of heterocyclic compounds have largely contributed to the development of theoretical ideas in organic chemistry and helped to solve the problems of producing novel compounds of practical value—pharmacological preparations, dyes, and intermediates for the synthesis of organic fine chemicals.

Chemistry of Organoelementary Compounds

A. N. Nesmeyanov defined organoelementary chemistry as organic chemistry extended to all elements. It has thus become an immense boundary region between organic and inorganic chemistry. Nesmeyanov notes that such boundary regions provide especially favourable soil for "growth points" of science.

Study of the first organometallic compounds was begun in the 1860s by A. M. Butlerov, A. M. Zaitsev, and E. Frankland with the development of organozinc synthesis. After Grignard had shown in 1900 the advantages of replacing zinc by magnesium, A. E. Arbuzov, N. D. Zelinskii, Zh. I. Iotsich, L. A. Chugaev, V. V. Chelintsev, V. S. Yavorskii, A. E. Chichibabin, and others conducted broad theoretical, experimental, and practical investigations on organomagnesium synthesis. In 1920 V. N. Krestinskii prepared isocrotylmagnesium bromide, and thus filled the gap in the sequence of magnesium derivatives differing in the degree of saturation of the carbon atom adjacent to the metal:

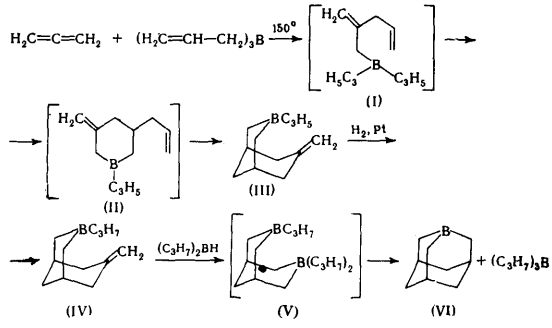
CH_3—MgX, RCH_2—MgX	R_2C=CH—MgX	RC≡C—MgX
(Grignard)	(Krestinskii)	(Iotsich)

Theoretical work has developed since the 1920s, and questions have been posed for the first time on the structure and chemical nature of Grignard reagents (N. V. Kondyrev, A. P. Terent'ev) and on the structure of the intermediate products and the mechanism of organomagnesium reactions (A. E. Arbuzov, B. A. Arbuzov, M. I. Konovalov, A. D. Petrov, T. I. Temnikova, A. N. Pudovik). Universal methods of quantitative analysis using organic derivatives of magnesium were elaborated by L. A. Chugaev and F. V. Tserevitinov.

A new field—the chemistry of organic compounds of the alkali metals—grew from P. P. Shorygin's discovery of the formation of sodium alkyls. Methods of preparation, structure, and reactions of organolithium compounds have been studied systematically by K. A. Kocheshkov. This worker elaborated methods for obtaining organocalcium compounds, which are of interest as components of catalysts for the polymerisation of unsaturated hydrocarbons and oxiran derivatives.

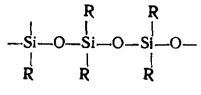
Nesmeyanov's discovery in 1929 of the diazo-method for preparing organomercury compounds started development of the chemistry of organic compounds of heavy metals (G. A. Razuvaev, M. M. Koton, O. A. Reutov, E. A. Shilov, I. P. Beletskaya, I. F. Lutsenko, Yu. K. Yur'ev, N. S. Zefirov).

Investigation of organic compounds of tervalent elements began with the preparation of aluminium and thallium derivatives by Nesmeyanov and Kocheshkov during the 1930s. The organic chemistry of aluminium and especially of boron has recently been intensively developed. New methods of synthesis and various reactions of organoboron compounds are being investigated by B. M. Mikhailov, L. I. Zakharkin, and O. Yu. Okhlobystin. Carborane derivatives are especially interesting as a promising basis for obtaining thermostable polymers. Spontaneous allylic rearrangement has been discovered in allylboron compounds. Condensation of acetylenic and allenic compounds with allylboranes is a new and effective method for the stereospecific synthesis of alicyclic compounds. The unique compound 1-boradamantane has been obtained, in which the boron atom is tetrahedral, in contrast to the usual boron trialkyls:



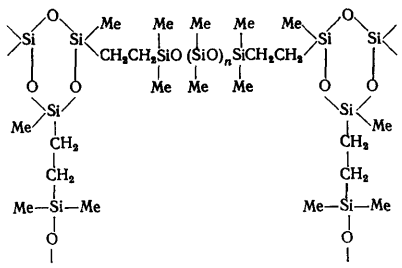
1-Boradamantane possesses several specific chemical and physical properties, in particular high complexing power with respect to various ligands, even those towards which boron trialkyls are inert. A new class of boron hydrides has been obtained—the borines—in which BH_3 is a functional group attached to a metal cation (V. S. Shpak).

The chemistry of silicon compounds had already attracted the attention of D. I. Mendeleev and A. M. Butlerov, the first to note the polymeric character of silicic acid. The ability to form polymers was a distinguishing feature of organosilicon compounds also. During the 1930s K. A. Andrianov first synthesised organosilicon polymers of the type

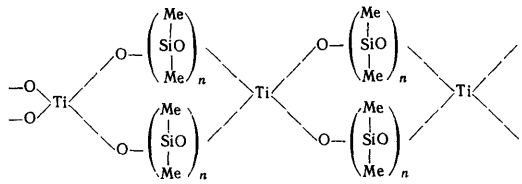


The interesting physicochemical properties of polyorganosiloxanes gave rise to numerous investigations in this

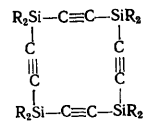
field. Hundreds of promising new compounds were obtained, e.g.



Recently efforts have been directed mainly at developing the preparation of new monomers of interest for obtaining polymers having specified properties—polysiloxanes of spirocyclic, spiral-staircase, and spirolinear structure, carbosilazanes, substituted vinylsilanes, organosilicon compounds containing other heteroatoms, e.g.

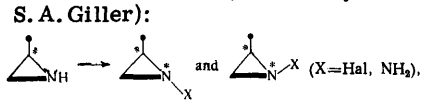


acetylenic silicon derivatives of the type



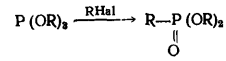
etc. The electronic interactions and special features of the silicon–heteroatom bond are being investigated, as well as the mechanisms and the kinetics of the reactions of organosilicon compounds and their biological activity (M. G. Voronkov). The chemistry of organic derivatives of the silicon analogues—germanium, tin, lead—is being explored.

Derivatives of Group V elements are being actively investigated. The long-standing stereochemical problem of synthesising systems with a non-inverting tervalent nitrogen pyramid has been solved in principle by the isolation of individual diastereomers of 2-substituted *N*-halogeno- and *N*-amino-aziridines (R. G. Kostyanovskii, Z. E. Samoilova, S. A. Giller):



Nitrogen in such compounds is comparable with the phosphorus atom in configurational stability.

The foundations of the chemistry of organic derivatives of phosphorus were laid by A. E. Arbuzov, who detected the rearrangement



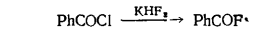
This became one of the chief methods for obtaining some classes of organophosphorus compounds. A new class of aromatic compounds containing a two-coordinated phosphorus atom has been discovered—the phosphadiazoles (A. I. Shvetsov-Shilovskii).

The biological activity of organophosphorus compounds is being studied, many of them finding application as medicinals and insecticides. The possibility of practical use as lubricants, plasticisers, and non-flammable polymers stimulates fresh synthetic exploration in this extremely important field of chemical science and practice.

The complex-forming properties of organophosphorus molecules are of great value, in particular enabling lead and beryllium to be removed from organisms. New principles have now been developed for enhancing the selectivity of organophosphorus complexing agents towards metal cations. Introduction into the molecule of fragments that fix sterically the orientation of donor atoms and the size of chelate rings yields highly efficient and selective new extractants, several of which are produced industrially and used in technical processes. Conditions have been worked out for introducing methylphosphonic groups at the nitrogen in triethylenetetramine and polyethylenimine to yield polymeric complexing agents.

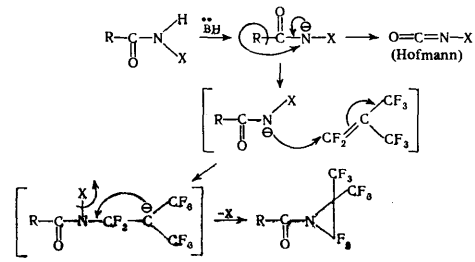
Organophosphorus ion-exchange resins have been synthesised. Methods are being sought for the directed synthesis of insecticides—derivatives of dithioic acids of phosphorus with peptide residues in the side-chain—which are relatively non-toxic to humans and animals, and do not leave toxic residues in the environment. New medicinals (diphenizide, hexaphosphamide, etc.) are being produced and introduced into clinical practice.

A young but vigorously developing field is the chemistry of organofluorine compounds, whose growth is due mainly to the work of I. L. Knunyants and his school (B. L. Dyatkin, L. S. German, Yu. A. Cheburkov, N. P. Gambaryan), N. N. Vorozhtsov, L. M. Yagupol'skii, A. Ya. Yakubovich, A. V. Fokin. In 1868 A. P. Borodin obtained the first fluorinated organic compound—benzoyl fluoride:



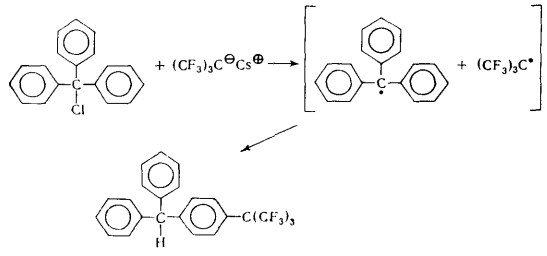
One of the chief general methods for introducing fluorine into an organic molecule—replacing a chlorine atom by fluorine by the action of a metal fluoride—was thus discovered. Fluorinated derivatives have now been obtained for almost all classes of organic compounds. Investigation of the structure, properties, and reactions of fluorinated organic compounds has introduced much that is new, often unexpected, into theoretical ideas in chemistry, and has had a widespread effect in experimental chemistry. Study of the nature of the π-bond in fluorinated alkenes, ketones, ketens, allenes, heterocumulenes, and aromatic compounds has led to the discovery of several unusual new rearrangements and reactions and to the synthesis of new types of compounds of practical importance.

The electronically amphoteric character of the double bond in fluoroalkenes is especially interesting, being responsible in several cases for reversal of the mechanism of addition of electrophilic and nucleophilic reactants. For example, the ability of fluoroalkenes to form anions under the influence of nucleophiles is used to intercept the hypothetical *N*-anion formed in the Hogmann, Curtius, etc. reactions:



The exceptionally strong basicity of the fluoride anion (e.g. in potassium and tetraethylammonium fluorides) in aprotic media has been observed for the first time. It greatly extends the opportunities for preparing various types of fluorinated organic compounds.

Great interest is taken in the chemistry of perfluorocarbanions, for whose study modern physicochemical methods are widely used. Thus the mechanism of the reaction of triphenylmethyl chloride with perfluoro-2-methylpropene in the presence of caesium fluoride, involving migration of the reaction centre, has been established from the variation in the concentration of the intermediate trityl radical measured by electron spin resonance:



Several new methods have been worked out for obtaining fluoro-organic compounds—concerted electrophilic addition to unsaturated systems in strong acids, anodic fluorination of aromatic compounds in organic solvents, and an industrial process for the direct fluorination of uracil to obtain 5-fluorouracil, an anti-tumour preparation —and hexafluorobenzene can be obtained from the more readily available hexachlorobenzene and potassium fluoride. A method has also been found for obtaining partly and completely fluorinated aromatic and heterocyclic compounds.

Processes have been developed for preparing compounds of types $Ar-ElF_n$ and $Ar-ElR_n^f$ (where El = Si, Ge, N, P, O, S, Se, I, Hg). In particular, compounds containing a pentacovalent iodine atom—aryl tetrafluoriodides—have been obtained for the first time.

The discovery and study of carbonyls of the metals—iron, nickel, and cobalt—preceded development of the chemistry of organic derivatives of transition metals. The discovery of ferrocene (dicyclopentadienyliron) began a new stage in organometallic chemistry—the study of sandwich compounds—for which the usual concepts of valency and coordination number have disappeared: here the atom of the transition metal is located between two rings, to which it is attached by a π-bond (Nesmeyanov and Razuvaev schools). Within a comparatively short time a detailed study of the reactivity of ferrocene had indicated its superaromatic character. Numerous substitutions in the cyclopentadienyl ring and reactions involving the iron atom gave rise to new classes of ferrocene compounds. Polymers based on ferrocene derivatives were obtained, including those containing silicon (A. D. Petrov, N. S. Nametkin, V. V. Korshak).

Physicochemical investigations of metallocenes were made by A. I. Kitaigorodskii, Yu. N. Sheinker, L. A. Kazitsyna, and the electronic structures of ferrocene and several other sandwich compounds were calculated by M. E. Dyatkina and E. M. Shustorovich. Cyclopentadienyl and cyclopentadienyl-carbonyl derivatives of manganese, rhenium, titanium, and other transition elements have been investigated. The chemistry of olefinic and acetylenic π-complexes of transition metals is represented by the work of Ya. K. Syrkin, B. A. Dolgoplosk, and I. I. Moiseev.

Complexes of transition metals find wide application in catalysis. Thus the compounds of graphite with low-valency palladium first obtained by M. E. Vol'pin proved to be promising catalysts for several organic reactions. A catalyst has been developed from allyl, acetate, and acetylacetonate complexes of palladium for chemical copper-plating in the manufacture of a self-cleaning foliated resin-impregnated laminated cloth for the printed circuits of high-speed electronic computers. Compounds of transition metals are used as catalysts for several novel reactions (synthesis of ammonia under mild conditions, synthesis of aromatic amines from hydrocarbons and molecular nitrogen, etc.). Lamellar compounds of graphite with several Group VIII transition metals, which are effective catalysts for the fixation of nitrogen and for the hydrogenation and isomerisation of alkenes and alkynes, have been obtained for the first time.

At the present time the chemistry of organoelementary compounds is developing along the lines of the synthesis of new compounds and fundamental research on their structure and reactivity as well as the mechanisms and the kinetics of the reactions.

Theoretical concepts are being shaped in the chemistry of organoelementary compounds. Thus the properties of organic compounds of Group V elements can be understood and predicted from the determination and calculation of the inversion barriers of the elements. In particular, a pyramidal configuration of nitrogen, phosphorus, and arsenic has been demonstrated in ethylenamines, acylphosphines, and acylarsines respectively, which disproves the long held view that they are completely analogous to ordinary amides (Kostyanovskii). During recent years a single system has been constructed for the $\sigma-\rho$ analysis of organophosphorus compounds, the electronic effects of substituents containing Groups IV–VI elements in the three-coordinated state have been studied, and quantum-chemical calculations have been made of certain specific molecules. A rebound mechanism has been suggested for the electrophilic isotope exchange of hydrogen in π-aromatic complexes of chromium and manganese. The structure of new types of compounds has been established by X-ray diffraction. Examination of the e.s.r. spectra of a number of organophosphorus radical-anions has proved unambiguously that the unpaired electron is delocalised over the substituents, and hence that the phosphorus atom is not an "insulating bridge" in the chain of conjugation (A. V. Il'yasov, Ya. A. Levin, I. D. Morozova).

E. I. Fedin developed research on the nuclear magnetic resonance spectra of organoelementary compounds under pulsed conditions (Fourier spectroscopy), which enabled spectra to be recorded not only at extremely low concentrations in solution but also for isotopes having a very small natural content (carbon-13, nitrogen-15, etc.) (Fig. 27). This produced a sharp increase in the information content of n.m.r. measurements in structural investigations and in study of the electronic characteristics of substituents. The SCAD phenomenon—statistically controlled association-complex diastereomerism—has been detected by Fourier $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Thus a solution of unequal concentrations of enantiomeric phosphorus-containing depsipeptides exhibited a doublet of the phosphorus-31 signal with an intensity ratio equal to the concentration ratio of the enantiomers (Fig. 28) (M. I. Kabachnik, T. A. Mastryukova, E. I. Fedin). This unexpected phenomenon opens up, in particular, prospects of investigating the detailed causes of stereospecificity in the action of biologically active substances.

Bio-organic Chemistry

Research on peptides and proteins began with the work of N. D. Zelinskii and his school. Effective methods were found for resolving and analysing such materials, while α-amino acids were obtained by the amination of halogenated acids and by the cyanohydrin reaction. The further development of the chemistry of proteins and peptides in the USSR, as throughout the world, has become increasingly closely interwoven with physicochemical and biochemical investigations.

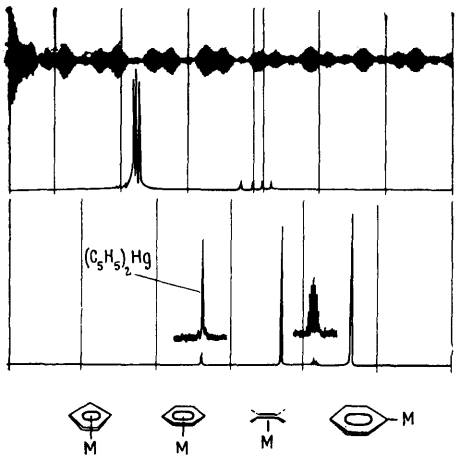


Figure 27. Fourier spectrum of ^{13}C n.m.r. with the natural content (1.1%) of the isotope.

Work on the chemical characteristics of complicated biopolymers has been directed at establishing the structure of glycoproteins (N. K. Kochetkov, V. A. Derevitskaya, E. D. Kaverzneva) and the primary structure of pepsin (V. M. Stepanov) as well as studying the biological role of enzymes (A. E. Braunshtein, V. N. Orekhovich, S. R. Mardashev, V. A. Belitser). Research is being undertaken with the aim of establishing effective new methods for analysing the primary structure of proteins and the sequence of amino-acid residues in peptides. The application of structural mass spectrometry (M. M. Shemyakin, Yu. A. Ovchinnikov, N. S. Vul'fson) has proved especially promising in this respect. Chromatographic procedures have been elaborated for separating and analysing complicated mixtures of amino-acids and methods for determining their optical purity (V. M. Belikov).

An important achievement has been the industrial production of the difficultly accessible hormone, insulin. A combined method has been worked out for separating the pituitary hormones (A. S. Khokhlov, F. Yu. Ryshka), and a technical synthesis of oxytocin and angiotensin (S. A. Giller, G. I. Chipen).

Methodical investigations are being made on the synthesis of amino-acids and peptides. A rapid new method has been suggested for obtaining polypeptides in aqueous medium without the isolation of intermediate products (D. G. Knorre), and also a new method of synthesising peptides on a polymeric carrier in solution (L. A. Shchukina). Priority is due to Soviet investigators in developing the chemistry of biologically important atypical peptides, in particular depsipeptides (M. M. Shemyakin, Yu. A. Ovchinnikov, E. I. Vinogradova). A new method has been discovered for synthesising linear and cyclic peptides and depsipeptides by the insertion of amino- and hydroxy-acyl groups into peptide systems (V. K. Antonov, A. M. Shkrob). The accumulation of empirical data deepens our understanding of the relation between the chemical structure and the biological character of peptides, which makes possible the directed synthesis of compounds having specified properties. During recent years extensive use has been made of physical methods in investigating polypeptides and proteins. Conformational analysis owes its progress to nuclear magnetic resonance (V. F. Bystrov), infrared spectroscopy (Yu. N. Chirgadze), optical rotatory dispersion, (V. T. Ivanov), X-ray diffraction (I. S. Andreeva, B. K. Vainshtein), and the combination of physicochemical methods with theoretical calculations (M. V. Vol'kenshtein, O. B. Ptitsyn).

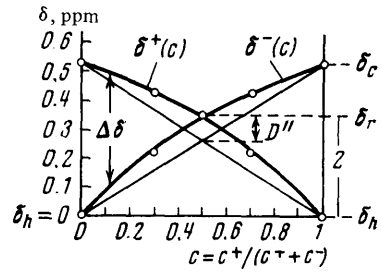
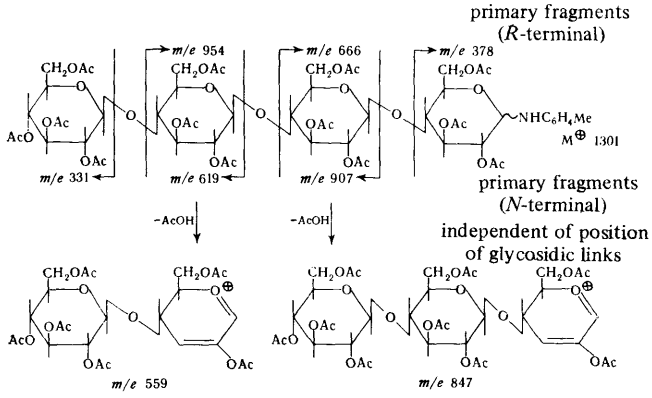


Figure 28. Dependence of ^{31}P chemical shifts (δ^+ and δ^-) of (+)- and (−)-ethoxymethylthiophosphinylthioglycolyl-valine on the concentration ratio $c^+/(c^+ + c^-)$.

The first work on the chemistry of nucleic acids included determination and comparison of the nucleotide composition of deoxyribonucleic acids in various lower and higher organisms, from which several characteristic features could be deduced (A. N. Belozerskii). A systematic search is being made for fundamental approaches to establishing the primary structure (i.e. the sequence of nucleotides), as yet in the simpler examples—transfer ribonucleic acids (A. A. Baev, D. G. Knorre). A promising way of studying the structure and functions of nucleic acids and their components is to modify them chemically, in particular with such specific agents as substituted hydroxylamines (N. K. Kochetkov, E. I. Budovskii). Compounds of nucleic acids with proteins are under investigation. Not only natural nucleoproteins but also model compounds with different types of amino-acid–nucleotide bond are being studied (M. A. Prokof'ev).

Development of the chemistry of carbohydrates in our country began with the work of P. P. Shorygin on the preparation of previously unknown cellulose ethers and esters, which was continued by A. E. Favorskii, S. N. Danilov, M. F. Shostakovskii, Z. A. Rogovin, N. I. Nikitin, M. M. Ushakov. Many studies were made of the degradation and oxidation of cellulose and other polysaccharides. The structure and the reaction mechanisms of starch, amyloses, glycogens, dextrans, etc. have been investigated. Much attention has been paid during the past two

decades to mono- and oligo-saccharides present in biologically important carbohydrate-containing polymers. Simple models of glycopeptides with various types of bonds have also been studied. The preparation and reactivity of carbohydrate phosphites and phosphinates—intermediates for the preparation of phosphorylated sugars—are being investigated (A. A. Petrov, E. E. Nifant'ev). Methods have been worked out for the synthesis of *C*-glycosides, in particular by applying the Wittig reaction to diverse phosphoranes (Yu. A. Zhdanov), and new methods of producing a glycosidic link (A. Ya. Khorlin, A. F. Bochkov, G. B. Elyakov). Effective methods are being developed for the structural analysis of carbohydrates. A mass-spectrometric method has been worked out for determining the sequence in oligosaccharides (see Scheme) (N. K. Kochetkov, O. S. Chizhov).



secondary fragments, the presence or absence of which depends on the position of the glycosidic links.

The chemistry of steroids has been investigated in the USSR since the 1930s, when M. I. Ushakov established the foundations of the synthesis of transformed steroids, in particular 6- and 16-methyl derivatives possessing strong physiological activity. The domestic manufacture of steroidal hormones based on cholesterol was established during the post-war period. In the 1950s work was begun in I. N. Nazarov's laboratory on a complete synthesis of steroidal compounds, and was developed by L. D. Bergel'son, I. V. Torgov, V. F. Kucherov, S. I. Zav'yalov, V. I. Maksimov. Microbiological and enzymatic transformations of steroids have been investigated by G. K. Skryabin and N. N. Suvorov.

Research on the synthesis of lipids has developed in several directions—the synthesis of natural fatty acids, the search for methods of synthesising glycerides and sphingolipids, and the synthesis of new types of phospholipids.

A thorough study of the most important branches of the chemistry of natural compounds enumerated above, together with the chemistry of antibiotics, vitamins, coenzymes, and alkaloids is being made in several institutes of the Academy of Sciences, among which the leading establishments are the Shemyakin Institute of Bio-organic Chemistry, Institute of Molecular Biology, Bakh Institute of Biochemistry, Protein Institute, Institute of Biological Physics, and Institute of the Biochemistry and the Physiology of Micro-organisms.

Systematic chemical and medico-biological investigations in the USSR resulted in the establishment of the present-day antibiotics industry, which produces all the most important antibiotics. Among the most significant chemical investigations on antibiotics are the discovery of chloramphenicol and its derivatives with the establishment of their structure (Shemyakin), the synthesis of cycloserine and study of the mechanism by which it functions (N. K. Kochetkov, R. M. Khomutov, M. Ya. Karpeiskii), determination of the absolute configuration of tetracyclines (M. N. Kolosov, A. I. Gurevich), elaboration of methods for the synthesis of penicillins and their analogues (I. L. Knunyants, I. T. Strukov, S. A. Giller), and general methods for separating mixtures of streptothricins (Khokhlov).

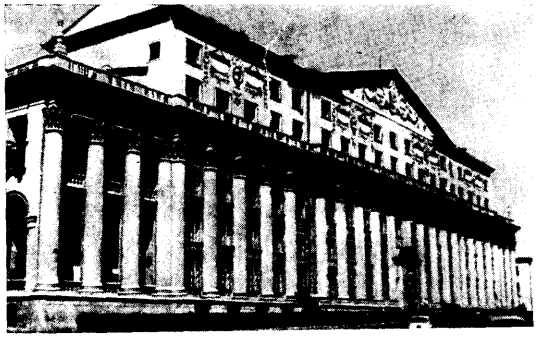
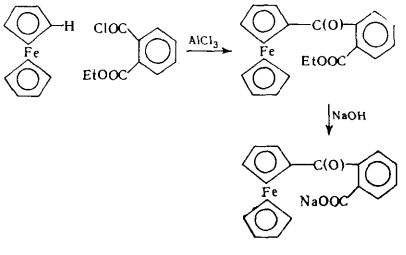


Figure 29. Shemyakin Institute of Bio-organic Chemistry of the USSR Academy of Sciences.

Studies of the chemistry of alkaloids, first begun by A. E. Chichibabin, were extended under the direction of A. P. Orekhov, N. A. Preobrazhenskii, A. S. Sadykov, S. Yu. Yunusov.

The complete structure has been determined for an important enzyme—the cytoplasmic aspartate aminotransferase from porcine heart muscle—containing 412 amino-acid residues (Fig. 30). This enzyme is one of the largest proteins whose structure has been deciphered (Ovchinnikov).

The achievements in the chemistry of natural compounds, together with advances in the organic chemistry of the most diverse classes of compounds, form the basis for such an important branch as the chemistry of medicinals and biologically active compounds. Among various new medicinal preparations mention must be made of ferroceron for the treatment of illnesses associated with an iron deficiency in the organism, e.g. iron-deficient anaemia of various aetiologies, ozaena, and paradentosis (A. N. Nesmeyanov). The active principle of ferroceron—sodium *o*-ferrocenylcarbonylbenzoate—is obtained by acylating ferrocene with ethyl *o*-chloroformylbenzoate:



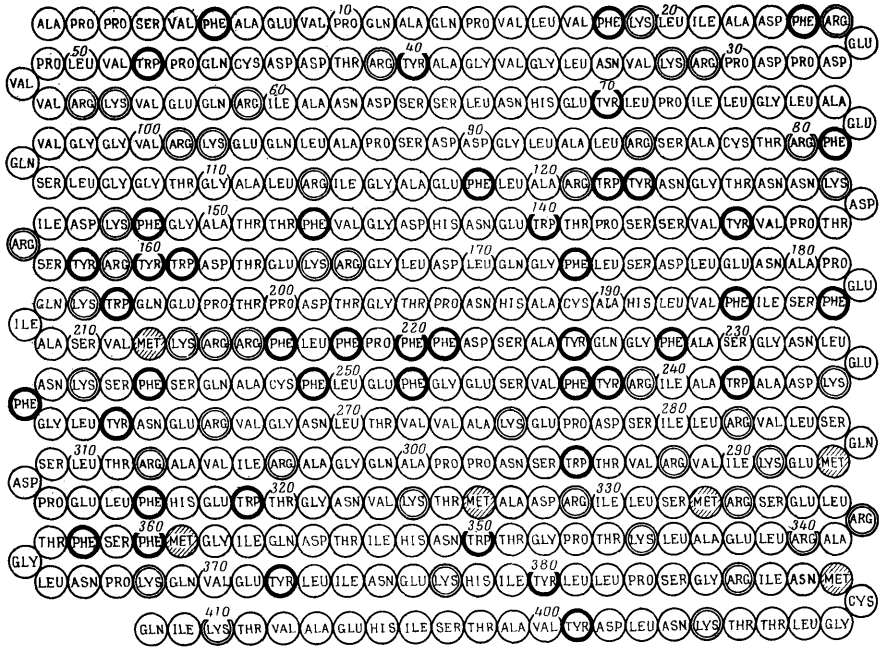


Figure 30. Amino-acid sequence of cytoplasmic aspartate aminotransferase from porcine heart muscle.

On Nesmeyanov's initiative the scientific foundations are being laid for the synthesis of artificial food—chemical and microbiological methods for the production of amino-acids, peptides, and proteins, research on the chemistry of odour and taste, study of the principles underlying the production of new types of foods. Recent years have seen the development of a convenient synthesis of DL-tryptophan by the cathodic reduction of indolylnitro-acrylates and their saturated analogues, conditions for the asymmetric synthesis of α-amino-acids in the proton exchange of racemic amino-acids on complex formation with metals of variable valency, and a synthesis of DL-glutamic acid, used as a flavouring agent (Belikov).

Convenient syntheses have been worked out for heterocyclic compounds of various structures, such as imidazolines, hydroxyhydropyrimidines, and dihydrotriazines, which are of interest with respect to their physiological activity (S. V. Rogozhin).

Petroleum Chemistry

Research on the chemistry of petroleum is associated with the names of D. I. Mendeleev, V. V. Markovnikov, N. D. Zelinskii, A. E. Favorskii, F. F. Beil'shtein [Beilstein], M. I. Konovalov, S. V. Lebedev, V. N. Ipat'ev, A. V. Topchiev, I. M, Gubkin, S. S. Nametkin. During the 1870–1890s Mendeleev studied Russia's oil-bearing deposits, foreseeing in petroleum an extremely valuable raw material for the production of organic compounds. He was the first to pose the question of the utilisation of natural gases, and put forward the idea of the subterranean gasification of coal. From the 1880s Markovnikov undertook a systematic study of petroleum, and proposed the name "naphthenes" for one of the types of hydrocarbons originating from petroleum. He isolated and identified many individual compounds, and studied their chemical and physical properties in comparison with model compounds. Zelinskii made many investigations on the interconversion of hydrocarbons, developed methods for the preparation of various compounds from petroleum raw material, and put forward a theory of the organic origin of petroleum.

Nametkin made investigations on the chemistry and technology of petroleum and natural gas. He elucidated a single mechanism for the nitrating and oxidising action of nitric acid on aliphatic and mono- and bi-cyclic hydrocarbons, studied the addition and the detachment of the elements of water and hydrogen halides to and from bicyclic compounds, as well as isomerisations of camphenic compounds, discovered the rearrangement bearing his name, and investigated the stereochemistry of mono- and bi-cyclic systems. Nametkin studied the composition of combustible natural gases and petroleums from various deposits, and investigated the chemical nature of solid hydrocarbons (paraffins and ceresins). He made various studies of oxidative cracking, catalytic aromatisation, the isomerisation of butenes into 2-methylpropene, and many other topics. He worked out valuable methods for analysing aromatic hydrocarbons, unsaturated hydrocarbons in gasolines produced by cracking, sulphur-containing compounds, and other compounds.

At the beginning of the century work on petroleum chemistry was conducted in college laboratories, mainly in Moscow University. The early years of the Soviet régime saw the foundation of specialised petroleum institutes, in which were elaborated the principles of several new manufacturing processes—the production of phenol and acetone, oxiran and methyloxiran, organic acids, alcohols, etc.—based on petroleum chemistry. The Moscow Petroleum-processing Works (directed by D. V. Ivanyukov) plays an important role in the introduction of new petroleum-chemical processes.

The main lines of development of petroleum chemistry are determined by the diverse tasks of present-day petrochemical production—study of the composition and properties of petroleums, establishment of scientific foundations for their processing and the production of various monomers, polymeric materials, synthetic rubber and fibres, surface-active agents and detergents, and solvents, and the synthesis of valuable chemical materials based on hydrocarbons. A large volume of research has been devoted to studying the composition of petroleums from different deposits (P. I. Sanin, A. F. Plate, G. D. Gal'pern, A. D. Petrov). Principles of a scientific classification of petroleums–combining chemical, geochemical, and technical aspects of the problem—have been formulated (A. A. Petrov, G. P. Kurbskii).

Hundreds of different hydrocarbons originating from petroleum have been identified. Chromatographic methods have been worked out for separating complex hydrocarbon mixtures, and also methods for isolating hydrocarbons having a certain structure. Many-sided investigations have been made of the interaction of complex compounds of metals of variable valency with hydrocarbons and non-hydrocarbon compounds of petroleum, which resulted in the suggestion of an original method for improving the quality of petroleum products (N. S. Nametkin).

A photochemical procedure has been worked out for isolating ash-forming elements from petroleums and petroleum products from various deposits in Georgia. It was shown that polycyclic aromatic hydrocarbons can sensitise the photochemical oxidation of naphthenes in mineral oils.

Organoelementary compounds present in petroleums—primarily organosulphur compounds (R. D. Obolentsev)—have been investigated. Yu. K. Yur'ev undertook the synthesis and spectroscopic examination of the many model thiolans required for the identification of those in sulphurous petroleums in the USSR. Studies have been made of the reactions involving cleavage of the thiophen and thiolan rings, which underly the industrial desulphurisation of petroleums.

A study has been made of the processes involved in pyrolysis, which is the chief industrial method for obtaining the main products—unsaturated and aromatic hydrocarbons—of petrochemical synthesis. In particular, a kinetic investigation has been made of the pyrolysis of alkanes in mixtures with alkenes, naphthenes, and alkylated arenes. The use of labelled atoms has enabled the dependence of the hydrogen concentration on the composition of the pyrolysable mixtures to be determined, and the elementary acts governing the interaction of hydrocarbons during pyrolysis to be elucidated (K. P. Lavrovskii, R. A. Kalinenko). Research is being conducted on a combined scheme for processing the liquid products of pyrolysis, involving the isolation of cyclopentadiene, methylcyclopentadiene, and aromatic hydrocarbons, together with the production of polymeric resins. A rapid process of thermal-contact pyrolysis has been elaborated which permits the efficient processing of all petroleum products, including crudes.

Carrying out chemical reactions in a plasma jet at 2000–3000°C is a promising method for obtaining several important petrochemical products (L. S. Polak). The topics studied in the field of plasma chemistry have been expanded significantly during recent years. The scientific foundations of a plasmachemical technology have been worked out—the production of acetylene and technical hydrogen from natural gas, unsaturated hydrocarbons from benzine and crude petroleum, and synthesis gas for the manufacture of vinyl chloride. These processes are in industrial operation at several chemical concerns.

The fundamental investigations by N. D. Zelinskii, B. A. Kazanskii, A. A. Balandin on the catalytic conversion of hydrocarbons formed the basis for a theory of hydrogenation and dehydrogenation catalysis and for introducing many reactions into practice. Highly efficient and selective catalysts have been developed, in particular for the hydrodemethylation of toluene and the dehydrocyclisation of hexane to produce benzene, and for the dehydrogenation of ethylbenzene to styrene. Mechanisms of the dehydrocyclisation of C_6–C_8 alkanes and alkenes have been studied. Processes of dehydrocondensation in the catalytic formation of resinous and carbonaceous products have been investigated (M. G. Gonikberg, M. I. Rozengart, I. I. Brusov, G. M. Marukyan, G. V. Isagulyants).

An economic process has been developed for the production of butadiene by the single-stage dehydrogenation of butane on an alumina–chrome catalyst (O. D. Sterligov). A palladium–zeolite catalyst has been developed for the isomerisation of hydrocarbons, a zeolite catalyst for the alkylation of benzene by alkenes, and catalysts containing added rare-earth metal oxides, which accelerate hydrogenation and dehydrogenation but produce no skeletal isomerisation (Kh. M. Minachev).

Research is being conducted on the use of π-allyl complexes of transition metals as polymerisation catalysts. Original catalytic systems have been created for the synthesis of *cis*-1,4-polybutadiene. New opportunities for stereospecific catalysis have been opened up. In order to obtain valuable chemical products, in particular novel monomers, broad investigations are being made on the dimerisation, codimerisation, oligomerisation, and co-oligomerisation of unsaturated hydrocarbons in the presence of combined catalysts (B. A. Dolgoplosk, B. A. Krentsel', G. A. Tolstikov, V. M. Vdovin, V. S. Aliev, M. M. Kaliberdo, V. S. Gutyrya).

New homogeneous catalysts, based on complexes of ruthenium, rhodium, palladium, and cobalt, have shown high selectivity: for example, it has been possible to hydrogenate *cis*-penta-1,3-diene to *trans*-pent-2-ene. Catalysts have been prepared comprising organometallic complexes of transition metals fixed to various carriers, including graphite (M. E. Vol'pin, B. A. Dolgoplosk, Yu. I. Ermakov).

Methods for the preparation of functional derivatives of hydrocarbons, especially oxygen-containing compounds, are being investigated. The principle of controlling liquid-phase oxidation by introducing so called stop-reagents—substances that convert reactive intermediates into compounds resistant to oxidation—has been developed (A. N. Bashkirov, V. V. Kamzolkin).

A combined study of the mechanisms of reactions occurring on fused iron catalysts, together with elucidation of the properties of the intermediate surface compounds, has enabled several catalytic syntheses to be predicted and accomplished (A. N. Bashkirov, Yu. A. Kogan, A. Ya. Rozovskii).

An industrially promising method—oxidative ammonolysis—for the preparation of nitrogen-containing derivatives of hydrocarbons has been applied to toluene, xylenes, pseudocumene, durene, and chlorinated hydrocarbons (S. D. Mekhtiev). A proposed process for obtaining acrylonitrile involves oxidative ammonolysis of propene on a fluidised catalyst bed (Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences).

A series of comparative studies have been made of the chemistry of cyclic and unsaturated hydrocarbons and of silico-hydrocarbons. Besides broadening our views on the reactivity of these analogues, these investigations led to the production of interesting new materials, showing promise for use in the petrochemical and metallurgical industries as well as in several other branches of the national economy (N. S. Nametkin).

A petrochemical development is the chemistry of additives for improving the cleansing, dispersing, anti-wear, and other properties of motor and special oils (P. I. Sanin, A. M. Kuliev). A polymeric additive has been produced to ensure that high-alkane petroleums can be pumped through pipelines (V. P. Mamaev).

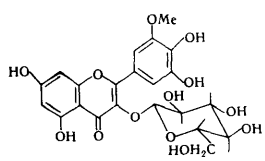
Chemistry of Wood

Significant results have been obtained in wood chemistry during recent years. The validity of regarding wood as a cross-linked polymer has been demonstrated. The number of cross-links in the cell walls of wood explains the changes in its properties and structure, which opens up the possibility of a purposeful variation in its properties.

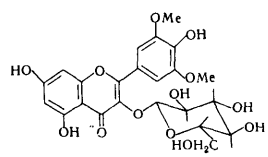
Phenolic phenylpropene compounds having a sulpho-group in the side-chain have been investigated as models of structural fragments of ligninsulphonic acids. The presence of the sulpho-group in this position is shown to stabilise the C_6–C_3 structural fragment of lignin. A procedure has been developed for preparing combined organic and mineral fertilisers based on hydrolytic lignin.

Application of salts of metals of variable valency permits controlled variation of the supermolecular structure and reactivity of cellulose (Institute of Physical Organic Chemistry of the Belorussian SSR Academy of Sciences). A technology is being worked out for a new nitric-acid method for obtaining cellulose, with use of the waste products as nitrogen-containing organic–mineral fertilisers. Fresh data have been obtained indicating that this method is promising for practical application.

Investigation of the interaction of levoglucosan with various di-isocyanates has shown that the hydroxypropylated material is suitable for the production of rigid polyurethan foams (Institute of Wood Chemistry of the Latvian SSR Academy of Sciences). Phenolic compounds from the needles, bark, and wood of conifer species of Siberia and the Far East have been studied. Two new compounds of the flavonoid series



laricitrin-3-β-D-glucopyranoside



laricetin-3-β-D-glucopyranoside

have been isolated from larch needles; they are of fundamental value for constructing a scheme of biogenesis for substances of this type (Irkutsk Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences).

Chemistry of Solid Fuels

M. V. Lomonosov, in his work "O sloyakh zemnykh [On the Earth's Strata]", formulated for the first time the view that coal is formed in stages from extinct plants, which have undergone the most complicated physicochemical transformations from wood through peat and lignite to coal.

An active part in establishing a science of fuel was taken by D. I. Mendeleev, V. V. Markovnikov, V. I. Vernadskii, N. D. Zelinskii, I. M. Gubkin, S. S. Nametkin, N. P. Chizhevskii, A. A. Skochinskii, Yu. A. Zhemchuzhnikov, N. M. Karavaev, A. B. Chernyshev, G. L. Stadnikov, A. F. Dobryanskii, and many others. The Committee on the Chemistry of Coal Tar and Coke, organised by the Academy of Sciences, did great work under the direction of A. E. Porai-Koshits and N. M. Karavaev. This Committee not only directed experimental work aimed at providing the growing organic synthetic industry with a continuous supply of raw material but also participated directly in studying the processes at undertakings with the aim of increasing the range of chemical products for organic synthesis based on the processing of coal.

An industrial classification of coals was worked out. The vast factual information that had accumulated on the qualitative characteristics of coals enabled native varieties to be differentiated according to their properties into power fuel for electrical generating stations and raw material for the production of high-quality coke with chemical products and materials (A. B. Chernyshov, N. G. Titov).

Studies were made on the possibility of expanding the raw-material base of coking by using abundant feebly coking coals. A theory of the formation of coke from mixtures of coals was put forward. L. M. Sapozhnikov's work on the thermal decomposition of coals and the formation of a plastic mass of carbon changed radically the view held on the effect of extreme temperatures, pressure, and oxidising and reducing media on structural changes in carbonaceous materials.

Theoretical researches were made on the genesis of coals, as a result of which new views were established on the nature of the geobiochemical processes involved in the transformation of plants into coal. A chemical theory was proposed for the formation of bogheads and the mixed humus–sapropelite origin of coals (Stadnikov). The petrological examination of coals has settled a wide range of questions concerning the classification and marking of coals, as well as the choice of raw material for industrial processing (Yu. A. Zhemchuzhnikov, I. I. Amosov, I. V. Eremin).

A fundamental scheme for the polymeric structure of the main organic substance in coals has been elaborated. It permitted generalisation of the concept of humic substances as monomeric molecular structures with fused aromatic rings and polyfunctional lateral substituents (V. I. Kasatochkin, L. L. Nesterenko). Great attention is paid to the thermal processing of coals, and catalytic methods for the hydrogenation and oxidation of hydrocarbons typical of the composition of fuels.

A procedure developed for the simultaneous hydrogenation of coal and a high-sulphur petroleum enables up to 50% of boiler fuel to be obtained with considerable quantities of motor fuel, phenols, benzene, and other chemical products (A. V. Lozovoi, A. A. Krichko). Promising methods have been studied for processing coals, peat, and bituminous shales by oxidation in alkaline medium with the production of various di- and poly-carboxylic acids (T. A. Kukharenko, A. S. Fomin).

The physicochemical and in particular thermodynamic investigation of the high-temperature processing of solid fuel led to an original method for the so called power-technical and power-chemical processing of fuel (A. B. Chernyshov, Z. F. Chukhanov). Chizhevskii carried out research with the aim of expanding the coal base of coking, and proposed an original design of coke-ovens.

Study of the distribution of rare elements and non-ferrous metals led to the so called "affinity series"

$$Ge > W > Ga > Be > Nb > Mo > Sc > Y > La > Zn$$

of these elements with respect to the organic matter in solid fossil fuels.

Processes have been worked out for obtaining a light porous filler (agloporite) for concrete by the heat-treatment of coal at 1100–1200°C.

The ion-exchange properties of peat can be increased by factors of 2.5–3 by oxidative degradation (N. I. Mitskivich, P. I. Bel'kevich, L. R. Chistova). The ammoniation of peat increases its moisture content, while its filtering power is diminished by factors of 10–15 (A. V. Tishkovich). Karavaev has completed many years of work on establishing the foundations of a general classification of fossil fuels.

Macromolecular Compounds

The chemistry of compounds of high molecular weight was founded as an independent branch at the beginning of this century. The concept of macromolecular substances as an important class of chemical compounds was due mainly to organic chemists. Research in this field began with the work of A. M. Butlerov, I. L. Kondakov, I. P. Ostromyslenskii, and P. P. Shorygin.

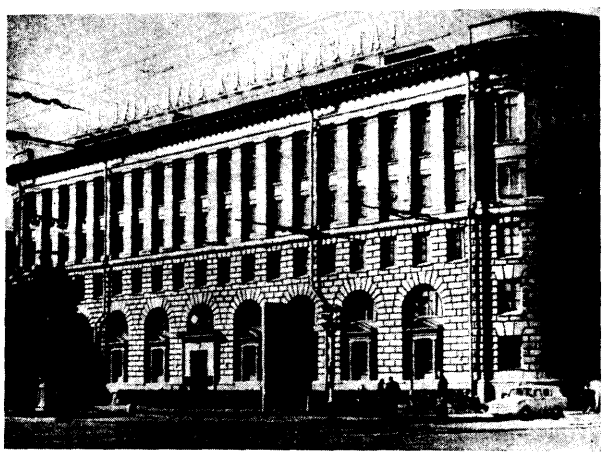


Figure 31. Institute of Macromolecular Compounds of the USSR Academy of Sciences.

S. V. Lebedev developed an industrial process for obtaining synthetic rubber based on butadiene. The study of polycondensation and polymerisation laid the foundations for the industrial production of phenol–formaldehyde resins, organosilicon polymers, synthetic rubbers, polymerisable oligomers, polymers for synthetic fibres, and other polymeric materials. Development of the science of polymerisation and isomerisation governed the growth of many branches of the chemistry of the monomers.

A. E. Favorskii, I. N. Nazarov, M. F. Shostakovskii suggested methods for obtaining ethynylvinylmethanols and vinyl ethers. These monomers have found wide application for the manufacture of various polymers and copolymers (adhesives, plasticisers, medicinals). K. A. Andrianov discovered convenient methods for the preparation of orthosilicic esters, and was the first to obtain polyorganosiloxanes, which have been widely used for the production of thermostable polymers employed for the thermal and electrical insulation of various articles, and the production of lubricants, plastics, rubbers, paints, and varnishes. Phosphorus-containing compounds (A. E. Arbuzov, B. A. Arbuzov, A. N. Pudovik, M. I. Kabachnik), organofluorine compounds (I. L. Knunyants), and various organoelementary compounds (A. N. Nesmeyanov) have been widely used for obtaining polymeric materials.

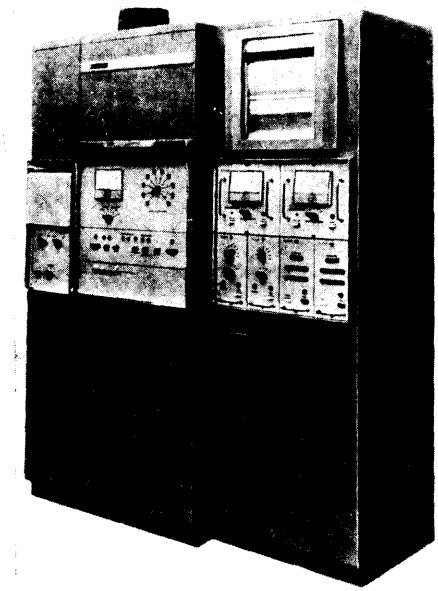


Figure 32. Automatic liquid chromatograph KhZh-1303 for determining molecular-weight distribution of polymers, developed by the Special Design Office of Analytical Instrumentation of the USSR Academy of Sciences and by the Institute of Macromolecular Compounds of the USSR Academy of Sciences.

The relations between the chemical structure and the reactivity of monomers have been studied. A new line of research began in the early 1960s, based on the possibility of varying the reactivity of monomers by complexing them with various substances. Investigations in this field, started by V. A. Kargin and V. A. Kabanov, offer the prospect of simulating the biosynthesis of polymeric compounds. The mechanisms of polymerisation and polycondensation have been investigated.

A theory of radical polymerisation and copolymerisation has been elaborated (S. S. Medvedev, Kh. S. Bagdasar'yan, A. D. Abkin). The kinetics and the mechanism of the redox initiation of chain polymerisation have been investigated (B. A. Dolgoplosk, E. I. Tinyakova), as well as the activation of radical polymerisation by complexing agents (V. A. Kargin, V. A. Kabanov, V. P. Zubov, E. B. Milovskaya, and others). Research on the elementary processes in the radical polymerisation of vinyl monomers and the cationic polymerisation of formaldehyde and oxirans led to the discovery of chain transfer (Medvedev) and of chain transfer with rupture (N. S. Enikolopov). These processes permitted control of the molecular weight, the molecular-weight distribution, and the structure of the polymers, and also enabled telomerisation to be accomplished (A. N. Nesmeyanov, R. Kh. Freidlina).

Broad investigations have been made of the uninhibited and inhibited heterophase polymerisation of polyfunctional monomers and oligomers to high degrees of conversion (G. P. Gladyshev, G. V. Korolev, N. N. Tvorogov). This work created a scientific basis for the industrial production and modification of several polymeric materials.

The influence of the supermolecular organisation of polymerising compounds on the kinetics of their conversion into chain and network polymers has been examined. Thus activation of the radical and ionic polymerisation of acrylic monomers and oligomers, due to a favourable arrangement of double bonds in liquid-crystalline and associated molecular aggregates of the liquid phase, has been detected and investigated (B. A. Krentsel', Yu. B. Amerik, N. N. Tvorogov, T. E. Lipatova), as well as in the crystallisation of monomers (V. A. Kargin, N. N. Semenov, V. A. Kalbanov, and others).

Work on polymerisation under extreme conditions has opened up a new line of research in the chemistry of polymerisation processes. Yu. S. Zaslavskii, A. A. Berlin, R. N. Zaslavskii, and M. I. Cherkashin investigated the polymerisation of various monomers and oligomers under the influence of friction, leading to the formation of polymer films which greatly diminished wear of the rubbing surfaces. N. S. Enikolopov and A. A. Zharov studied polymerisation under ultra-high pressure with shear. Work has been done on polymerisation in shock waves.

The mechanism of cationic polymerisation was first discussed by M. D. L'vov, G. G. Gustavson, and I. L. Kondakov at the end of the nineteenth century. S. S. Medvedev, A. R. Gantmakher, B. L. Erusalimskii investigated the mechanisms of the polymerisation of many unsaturated compounds in the presence of cationic catalysts, and in particular revealed the role of alkene–catalyst π-complexes. Specific aspects of the cationic polymerisation of rings appeared in papers by N. S. Enikolopov, S. G. Entelis, E. B. Lyudvig, and others.

Work on anionic polymerisation was begun by Lebedev, who made use of observations by A. A. Krakau and I. L. Kondakov that polymerisation might be accomplished in the presence of metallic sodium. The labours of S. S. Medvedev, A. R. Gantmakher, A. A. Korotkov, B. L. Erusalimskii elucidated many aspects of the kinetics and the mechanism, and established the effect of the nature of the alkali metal on the composition and structure of the polymers.

Studies of ionic telomerisation (A. A. Petrov, A. L. Klebanskii, M. F. Shostakovskii) yielded valuable products finding industrial application as polymeric materials.

Stereospecific polymerisation was studied by S. S. Medvedev, A. A. Korotkov, A. V. Topchiev, B. A. Dolgoplosk, E. I. Tinyakova, N. M. Chirkov, B. A. Krentsel', G. A. Razuvaev. The role of cobalt and titanium compounds in composite catalysts was established, and several novel catalytic systems were suggested, including π-allyl complexes for the polymerisation of diene hydrocarbons.

K. A. Andrianov, V. V. Korshak, S. R. Rafikov, L. B. Sokolov, S. V. Vinogradova made series of investigations on the mechanism of equilibrium and non-equilibrium polycondensation, revealing the effects of excess of reactants, simultaneous reactions, and experimental conditions on the mean molecular weights and the molecular-weight distribution. Berlin investigated the polycondensation of diols, polyols, and dibasic acids (or their derivatives) in the presence of unsaturated monobasic acids, and from the results worked out a general synthesis of polymerisable acrylic oligomers with terminal or regularly repeating reactive groups (condensation telomerisation). This work formed the scientific basis for the industrial production of several high polymers (polyamides, polyesters) and polymerisable oligomers (oligo(ether–acrylates) and their analogues).

The mechanism and the kinetics of the polyaddition of di-isocyanates to diols to form polyurethans have been studied (Yu. L. Spirin, T. E. Lipatova, S. G. Entelis, and others).

The development of such methods for synthesising polymers as oxidative dehydropolycondensation, polydiazotisation, polycoordination, polycyclisation, etc. led to the production of highly thermostable polymers having a system of conjugated aromatic and heterocyclic rings and exhibiting semiconductor and catalytic properties (V. V. Korshak, A. M. Sladkov, B. A. Krentsel', B. E. Davydov, Ya. M. Paushkin, I. L. Kotlyarevskii, A. A. Berlin, B. I. Liogon'kii, M. I. Cherkashin).

Among work promoting the industrial production of polymeric compounds and materials based on them mention must be made of investigations on the polymerisation of ethylene associated with the names of V. N. Ipat'ev, M. S. Nemtsov, A. I. Dintses, establishment of scientific principles for the manufacture of polypropylene (A. V. Topchiev, N. M. Chirkov, B. A. Krentsel'), and the production of Soviet synthetic rubbers (B. A. Dolgoplosk, A. I. Yakubchik, A. A. Korotkov, V. F. Evstratov).

Research aimed at obtaining poly(vinyl chloride) was initiated in our country by Ostromyslenskii in 1912. Development of this work led to organisation of the industrial production of polymers and copolymers of vinyl chloride. The work of S. M. Ushakov and P. P. Shorygin stimulated the industrial manufacture of polystyrene and poly(vinyl acetate), while the studies by G. S. Petrov mentioned above formed the basis for the production of phenol—formaldehyde and urea—formaldehyde resins and plastics. The industrial production of polyamides and aromatic polyesters is based on investigations by V. V. Korshak, I. L. Knunyants, Z. A. Rogovin, A. N. Nesmeyanov, R. Kh. Freidlina, A. A. Strepikheev, and others.

Compositions of oligomers with raw rubbers and thermoplastics were developed which enabled new industrial methods to be established for obtaining and modifying cured rubbers, elastomers, reinforced plastics, coatings, sealants, and other polymer materials (A. A. Berlin, A. S. Kuz'minskii, G. N. Petrov, I. S. Al'shits, M. S. Akutin, I. Ya. Kaplunov, and others).

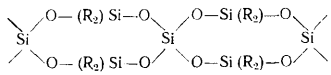
Study of the mechanochemistry of block and graft copolymerisation and reactions in the polymer chains laid the foundations for the industrial manufacture of highly impact-resistant polystyrene and poly(vinyl chloride), modified cellulosic fibres and cloth, and several other polymeric materials. Advances in the vulcanisation of

elastomers were due to original investigations by B. P. Zhukov, B. A. Dogadkin, and others.

A new field of polymer science—the chemistry of conjugated polymers—was opened up. Specific aspects of the supermolecular organisation and properties of these polymers were revealed, and the presence was demonstrated of low-lying triplet levels and paramagnetic centres influencing their reactivity and electrophysical properties (A. A. Ovchinnikov, L. A. Blyumenfel'd, A. A. Berlin, and others). The practical importance of these polymers is due to their use as photosensitive materials, organic semiconductors, inhibitors of the high-temperature degradation of elastomers and rigid-chain polymers, structural modifiers, and starting points for obtaining highly thermostable plastics.

Organosilicon polymers have acquired especial value among organoelementary polymers because of their astonishing combination of useful properties, high heat and frost resistance, excellent dielectric characteristics, good adhesive properties, absence of toxicity, etc. In 1937 Andrianov obtained the first patent in the world for the practical application of organosilicon compounds, and in 1940 he developed an industrial method for obtaining silicon tetrachloride—the most important starting material for the synthesis of polysiloxanes—by the reaction of chlorine with 35–65% ferrosilicon at 200°C. The mechanism of the formation of substituted orthosilicic esters was studied. Choice of a progressive technical procedure for obtaining organochlorosilanes in a fluidised bed enabled the large-scale industrial manufacture of methyl-, ethyl-, and phenyl-chlorosilanes to be organised.

The products of the simultaneous hydrolysis of di- and tri-functional organochlorosilanes were regarded as having a cyclolinear structure. The cohydrolysis of organochlorosilanes with aluminium chloride in alkaline media was used to obtain polyorganoaluminosiloxanes. Organospirocyclosiloxanes with the organosiloxane groups occupying a specified position in the spirocyclic ring



were prepared. Manufacture of a large range of organosilicon monomers and polymers was set up.

Study of the degradation and stabilisation of polymers was begun by S. V. Lebedev, B. A. Dolgoplosk, G. A. Razuvaev, V. A. Kargin, M. B. Neiman, A. S. Kuz'minskii. Kinetic investigations of the aging and stabilisation of polymers have been made by A. L. Buchachenko, G. P. Gladyshev, E. T. Denisov, V. V. Ershov, G. E. Zaikov, V. B. Miller, E. G. Rozantsev, D. Ya. Toptygin, V. Ya. Shlyapintokh, Yu. A. Shlyapnikov, and others. Studies have been made of the kinetics of oxidative degradation, the action of various stabilisers on the oxidation of polymers, and the synergic effect of several inhibitors. It has been discovered that chemical compounds that react rapidly with oxygen (or free radicals) to form inert products are able, when generated in polymer compositions or articles (as a result of the transformation of inert substances), to stabilise the polymeric materials against oxidative and/or thermal degradation at 300–400°C and above (Fig. 33).

Various iminoxyl radicals have been prepared which are widely used as "labels" and have proved effective stabilisers for several polymers. Work is being conducted on modifying the polymers to prolong the "life span" of polymeric compositions (N. S. Enikolopov, S. R. Rafikov, Z. A. Rogovin, Kh. U. Usmanov, N. A. Plate, and others).

The first investigations on the physical chemistry of polymers were aimed at studying their mechanical properties taking into account relaxation phenomena accompanying deformation and fracture. The results formed the basis of the contemporary physical chemistry of polymers (A. P. Aleksandrov, P. P. Kobeko, Yu. S. Lazurkin, V. A. Kargin, G. L. Slonimskii, M. V. Vol'kenshtein, S. E. Bresler, S. Ya. Frenkel', E. V. Kuvshinskii, G. I. Gurevich).

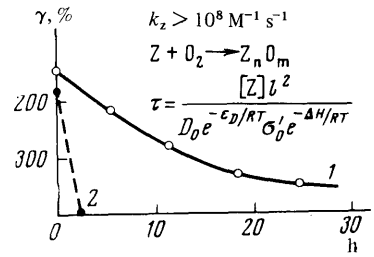


Figure 33. Stabilisation of thermostable polymers—variation in relative elongation at rupture for cured rubber based on SKTV-2 when aged in air (350°C): 1) stabilised specimen; 2) control.

The usual concepts valid for solutions of compounds of low molecular weight are shown to apply also to solutions of polymers. V. N. Tsvetkov investigated the latter in order to obtain information on the structure and conformation of the soluble molecules. A. A. Tager, V. P. Zubov studied the thermodynamics of the solutions, swelling, plasticisation, and gel formation. Research on the rheology of polymers was begun and developed by P. A. Rebinder and G. V. Vinogradov.

A. N. Zhurkov, G. M. Bartenev, V. E. Gul', A. L. Rabinovich, Yu. M. Malinskii developed theoretical ideas on the nature of the deformability and strength of polymers and reinforced plastics, and also studied the relaxation properties of polymers having rubberlike elasticity. V. A. Kargin and T. I. Sogolova established methods for modifying the supermolecular structure and physicomechanical properties of polymers.

Aspects of the physical chemistry of surface phenomena in polymer systems have been investigated by Yu. S. Lipatov, Yu. A. El'tekov, while the foundations for a theory of adhesion have been laid by B. V. Deryagin, V. E. Basin, S. S. Voyutskii. These investigations are not only of great theoretical importance but also of practical value, especially for the controlled production of adhesives, protective coatings, binders, reinforced plastics, etc.

INORGANIC CHEMISTRY

The inception of quantitative investigations on inorganic chemistry is connected with the work of M. V. Lomonosov. During the eighteenth century information accumulated on the composition and properties of various substances, and new elements were discovered. The establishment of the atomic—molecular doctrine in the nineteenth century, the discovery of the stoichiometric laws of chemical reaction, and the formulation of such concepts as atom, equivalent,

molecule, and valency enabled a start to be made in elaborating theoretical principles of inorganic chemistry.

D. I. Mendeleev's discovery of the Periodic Law and the Periodic System of the elements (1869) initiated a new stage in the development of chemistry. The discoveries of physics at the beginning of the twentieth century—the detection of radioactivity, the composite structure of the atom, and the quantum theory of atomic structure—faced inorganic chemistry with the task of studying the structure of atoms and molecules, and relating such structure to chemical properties.

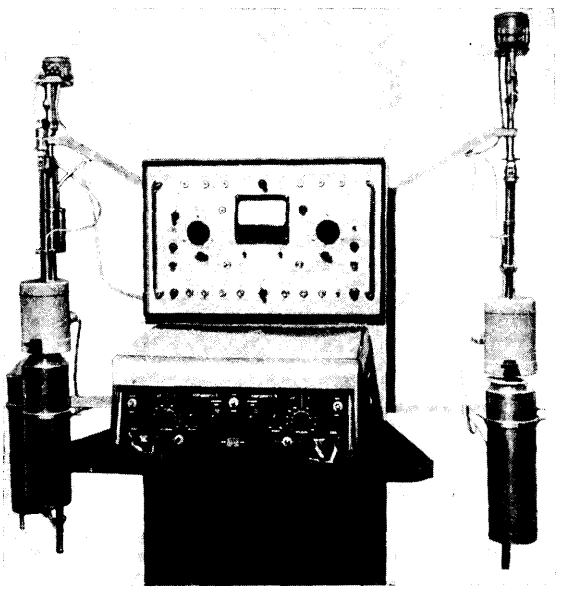


Figure 34. Automatic equipment for recording thermomechanical properties of polymers, developed in the Arbuzov Institute of Organic and Physical Chemistry of the USSR Academy of Sciences.

The Institute of Physicochemical Analysis, of which N. S. Kurnakov became director, and the Institute of Platinum under the direction of L. A. Chugaev were organised in Petrograd in 1918. These establishments were combined in 1934 with the Laboratory of General Chemistry as the Institute of General and Inorganic Chemistry. The Scientific Research Institute of Fertilisers, Insecticides, and Fungicides and the Institute of Chemical Reagents were founded in 1919, the State Institute of Applied Chemistry was established in 1920, and the Radium Institute headed by V. I. Vernadskii in 1922. Many other institutions and laboratories, concerned with all aspects of inorganic chemistry, were established in subsequent years.

Modern inorganic chemistry makes widespread use of the achievements of other branches of chemistry, the theoretical concepts and methods of physics, crystallography, crystal chemistry, and the theory of molecular structure. The principal fields of inorganic chemistry which have been most fully developed are—the chemistry of simple inorganic compounds, the chemistry of metals and alloys, the chemistry of the rare elements, radiochemistry, the chemistry of complex compounds, the chemistry of semiconductors, the chemistry of natural salts, and quantum inorganic chemistry.

Chemistry of Simple Compounds

Research on the chemistry of simple compounds came to be concerned with the structure and chemical properties of almost all elements and their simplest compounds. N. S. Kurnakov introduced the concepts of a chemical species, phases of variable composition, daltonides, and berthollides, and suggested the construction of equilibrium diagrams to represent the properties and stability of a chemical compound. Physicochemical analysis was used to study many of the simplest inorganic compounds; the unity of construction of diagrams for substances of different classes was demonstrated, compounds of unusual valency were detected, the wide distribution of phases of variable composition was established, and geometrical methods were developed for representing chemical systems (N. P. Radishchev, V. Ya. Anosov, A. G. Bergman, M. I. Ravich).

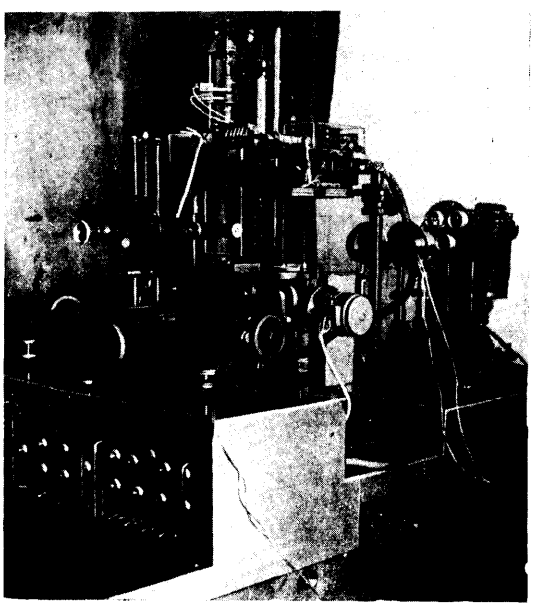


Figure 35. Opticomechanical apparatus for studying relaxation and creep in polymers (Arbuzov Institute of Organic and Physical Chemistry of the USSR Academy of Sciences).

During the 1930s physicochemical analysis became an objective method for studying complicated systems. Metals and alloys were investigated (V. A. Nemilov, N. V. Ageev, G. G. Urazov, V. I. Mikheeva), molten salts (A. G. Bergman, N. K. Voskresenskaya, N. S. Dombrovskaya, N. P. Luzhnaya), and multicomponent aqueous salt systems (V. I. Nikolaev, I. N. Lepeshkov). The chlorine metallurgy of rare and non-ferrous metals has been developed on the basis of the physicochemical analysis of systems involving chlorides of multivalent elements (G. G. Urazov, I. S. Morozov, and V. I. Evdokimov).

Methods of preparation of compounds of light elements, perchloric acid and its derivatives, hydrides of transition metals, hydroborons and their derivatives, etc. have undergone considerable development (S. Z. Makarov, A. F. Zhigach, V. I. Mikheeva, V. Ya. Rosolovskii, and others).

Many peroxides and ozonides have been obtained by I. I. Vol'nov. A series of investigations of the branched-chain decomposition of perchloric acid were made by V. Ya. Rosolovskii and G. B. Manelis.



Figure 36. Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences.

A new class of compounds—complex aluminium hydrides $AlH_3.nBH_3.mZ$, where Z is a nitrogen- or oxygen-containing ligand—have been prepared and subjected to physicochemical investigation at Moscow State University. These compounds were shown to be effective reductants and components of catalytic systems of the Ziegler–Natta type.

A. V. Novoselova has prepared novel polymeric beryllium alkoxoacetates $[Be(O.CO.CH_3)OR]_n$, as well as oxy- and hydroxy-acetates. Magnesium alkoxide halides have also been prepared, as promising catalysts for polymerisation processes.

The possibility of almost complete thermal dissociation of naturally occurring phosphates to give phosphorus pentoxide has been demonstrated by S. I. Vol'fkovich.

I. V. Tananaev, N. S. Nikolaev, and Yu. A. Buslaev have obtained important results on the acid–base equilibria of fluorides with hydrofluoric acid. A method developed for obtaining single crystals of copper(I) chloride gave a transparency equal to those of the best specimens in the world. Tungstates of thallium, barium, strontium, and the rare elements have been prepared and studied. Fluorides of Groups I–VI elements, oxofluorides, and polymeric fluorides have been studied by X-ray electron spectroscopy. Per-rhenates of copper, nickel, and lead have been prepared, as well as various barium chromates, niobates, and tantalates.

Developments have occurred in the chemistry of semiconductors (N. P. Sazhin) and dielectrics, and the chemistry of rare, trace, and rare-earth elements (I. V. Tananaev, K. A. Bol'shakov).

This is by no means a complete list of current researches on the preparation and properties of simple inorganic compounds.

The use of physical methods—X-ray diffraction, spectral methods of studying magnetic properties—is being developed in such investigations.

Methods have been elaborated for obtaining the pure metals necessary for radio-engineering and semiconductors. Under the direction of Yu. A. Zolotov investigations have been made on the extraction of more than twenty non-ferrous and noble metals by sulphur-containing organic compounds. Selective extractants have been proposed for copper, thallium, silver, and certain other metals both in the laboratory and in industrial use. Mixtures of a neutral and a cationic extractant have proved effective for the separation of transplutonic elements from rare-earth metals. L. F. Kuzina has worked out a new hydrogen-free process for the industrial production of metallic technetium.

Metals and Alloys

Many of the rules of alloy formation, methods of study, and preparation of alloys with valuable properties were first discovered and formulated by D. I. Mendeleev, N. S. Kurnakov, A. A. Baikov, P. M. Anosov, L. K. Chernov, E. S. Fedorov, A. A. Bochvar, A. A. Rzheshotarskii, and many others. An important aspect of the chemistry of metals is the character of their interatomic bonding. N. V. Ageev investigated the distribution of electron density in the interionic space, and showed that metals are bound by a continuous transfer of the electron cloud from one atom to the other.

Kurnakov established that the chemistry of alloys is the chemistry of continuous proportions: i.e. phases of variable composition (solid solutions) are formed, in which the component concentrations vary continuously. The properties of alloys are a continuous function of the component concentrations. The filling by electrons of energy bands in metallic crystals also obeys special rules.

The relation between the properties of metal—metal systems, in particular the heats of formation, and the structure of their electron shells has been shown in the work of Yu. M. Golutvin. The band theory (S. T. Konobeevskii) was of great value for understanding the solubility limits of metals one in another and the possibility of the formation of solid solutions. Research on the solid solutions formed in metallic systems was carried out over many years by N. S. Kurnakov, G. G. Urazov, N. I. Stepanov, A. T. Grigor'ev, V. A. Nemilov, P. Ya. Sal'dau, N. Kh. Abrikosov, O. S. Ivanov, I. I. Kornilov, V. I. Mikheeva, and many other scientists. It was shown that dissolution of the components in the formation of solid solutions is a special form of chemical interaction, and that this is accompanied in all cases by the evolution of heat owing to the formation of a chemical bond between atoms of the solute metal and molecules of the solvent.

Reactions occurring in solid solutions have been studied that lead to changes in the physical, mechanical, and other properties of the alloys (N. V. Ageev, A. A. Bochvar, S. A. Pogodin, V. N. Anosov, E. M. Savitskii, N. V. Grum-Grzhimailo, G. I. Chufarov). It was established that necessary conditions for the formation of solid solutions are isomorphism of the crystal structures of the separate components, similarity in size of their atoms, and a certain ratio of the electronegativity and ionisation potentials. A classification of solid solutions has been made.

The properties of solid solutions are currently being investigated in the Institute of General and Inorganic Chemistry, the Institute of Silicate Chemistry of the USSR Academy of Sciences, the Institute of Chemistry of the Ural Science Centre, and other institutions. It has been shown in particular that the ternary "alloy" based on zirconium dioxide ZrO_2–Y_2O_3–Nd_2O_3 possesses valuable electrophysical properties and refractoriness, and can be

recommended for the preparation of high-temperature electrodes of magnetohydrodynamic (MHD) generators (E. K. Keller). The properties of the hafnium dioxide–magnesium oxide system, which possesses high electrical conductivity, are being studied. A series of investigations is being made on the interaction, variation in composition of compounds, and polymorphic transitions in systems formed by alkali and rare-earth metal tungstates and molybdates. The solubility of magnesium, calcium, aluminium, lanthanum, neodymium, and zirconium oxides in $NaF-MgF_2$ melts and of lanthanum oxide in the $NaF-MgF_2(CaF_2, SrF_2, BaF_2)$ systems is under investigation.

Methods for the preparation and separation of novel compounds with special properties are being elaborated. The number of intermetallic compounds studied—binary, ternary, and multicomponent—has now reached 10 000; compounds of metals with non-metals—oxygen, hydrogen, nitrogen, silicon, boron, carbon—are also under investigation. Many of them possess special properties such as superconductivity, high-temperature strength, and hardness. A method has been worked out for obtaining intermetallic compounds with specified electrical and mechanical properties. Especially hard alloys are based on carbides of different metals—tungsten, titanium, cobalt, molybdenum, iron, etc. (N.S. Umanskii, G.V. Samsonov, V.I. Eremenko, I. I. Frantsevich, V. E. Ivanova, and others). A process has been worked out and realised under industrial conditions for the production of titanium carbonitride, from which can be obtained alloys at least as hard as those based on tungsten carbide.

Methods have been elaborated for the low-temperature preparation of oxonitrides, oxophosphides, and oxoborides of several transition metals (Yu. A. Buslaev). The properties of molybdenum disilicide, which possesses enhanced high-temperature strength, have been studied, and the production of heaters for high-temperature furnaces has been established.

A. G. Merzhanov proposed the self-propagating high-temperature synthesis method to obtain refractory compounds. Table 1 lists compounds of different classes obtained by this method (more than seventy are known), and shows that almost all of them possess properties such as heat resistance, chemical stability, hardness, etc. that are important for practical application. Compounds having melting points above 3500°K—TaC, HfC, NbC, ZrC, HfN, TaB_2—are especially interesting. A method has been worked out for obtaining zirconium carbide, one of the main constructional materials in nuclear technology. Conditions have been found under which the product has a high degree of purity.

Metallic compounds exhibiting superconductivity at the temperature of liquid helium are of great interest; about a thousand such compounds are known at the present time.

[Quantum Inorganic Chemistry]

The quantum chemistry of inorganic compounds is a young branch of inorganic chemistry, which has greatly developed only during recent years. Work in this field is done at the Institute of General and Inorganic Chemistry and the Institute of New Chemical Problems of the USSR Academy of Sciences, the Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, the Institute of Chemistry of the Moldavian SSR, and other establishments.

During the 1950–1960s Ya. K. Syrkin and M. E. Dyatkina put forward several principles to form the basis for the further development of theoretical inorganic chemistry. Aspects of the participation of unshared pairs and vacant orbitals in chemical bonding were studied, a critical analysis was given of the concept of effective charge, and questions of chemical reactivity were considered.

Table 1. Compounds obtained by "spontaneously propagated high-temperature synthesis".

Compounds	Group in Periodic Table (metals)							Principal properties
	II	III	IV	V	VI	VII	VIII	
Nitrides	Mg_3N_2	BN AlN	TiN, ZrN, HfN	VN, NbN, TaN, Ta_2N	—	—	—	heat resistance, super- and semi-conductivity, chemical resistance, electrical and thermal insulation
Carbides	—	—	TiC, ZrC HfC, SiC	VC NbC, NbC, Nb_2C, TaC	WC	—	—	high m.p., great hardness, abrasives
Borides	MgB_2, MgB_4, MgB_6	—	TiB, TiB_2, ZrB_2, ZrB_4 HfB,	VB, VB_2, NbB, NbB_2, TaB, TaB_2	CrB, CrB_2, MoB, Mo_2B, MoB_2, Mo_2B_5, WB, W_2B, WB_2	MnB	FeB NiB	resistance to molten metals, abrasive, small capture cross-section for neutrons
Silicides	—	—	TiSi, TiSi $ZrSi$, $ZrSi_2$	—	$MoSi_2$	—	—	high resistance to high-temp. oxidation
Chalcogenides			TiSe	$NbSe_2$, $TaSe_2$	MoS_2, $MoSe_2$	—	—	highly antifrictional
Solid solutions	TiC—WC, Ni—Al, MoS_2—NbS_2, BC—BN, NbC—NbN, TiC—TiN, TaC—TaN, TiB_2—MoB_2, $Nb_xZr_{1-x}C_yN_{1-y}$							great hardness, superconductivity, antifrictional

Calculations of coordination compounds by the method of molecular orbitals were initiated in the Structure Laboratory of the Institute of General and Inorganic Chemistry. Calculation of the ferrocene molecule (M. E. Dyatkina, E. M. Shustorovich) was an important stage in the development of a native quantum chemistry. The first non-empirical programme in our country for calculations of inorganic compounds by means of an electronic computer was worked out in the same laboratory jointly with the Lomonosov Moscow Institute of Fine Chemical Technology (M. E. Dyatkina, N. M. Klimenko, V. K. Belov, E. L. Rozenberg). Many fluorides and oxy-anions of non-transition elements have been calculated by means of this programme, which is used in several Soviet and foreign laboratories.

In the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences a theory is being developed and systematic investigations are being made on X-ray-electron and X-ray spectra (V. I. Nefedov). Calculations are being made of the electronic structure of inorganic crystals (A. A. Levin).

In the Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, under the direction of K. B. Yatsimirskii, a series of studies have been made on the application of crystal-field theory to atoms having f-electrons, experimental and theoretical work has been done on the interaction of ligands, and the role of the symmetry of the last occupied and first vacant molecular orbitals for the physicochemical characteristics of inorganic compounds has been established. In the Institute of Chemistry of the Moldavian SSR systematic investigations are being made on vibronic interactions, and chemical aspects of the Jahn–Teller effect are being studied (I. B. Bersuker). Calculations of atomic orbital energies have been made in the Institute of New Chemical Problems, and the results have been used to analyse the stereochemistry and thermodynamics of inorganic compounds.

Comprehensive calculations have been made on the fluorides of the inert gases (O. P. Charkin).

Increasing attention is now being paid to quantum-chemical calculations. Quantum chemistry provides the theoretical foundation for interpreting the results of physical investigations on inorganic compounds.

Crystal Chemistry

The development of crystal chemistry in our country is associated with the names of A. E. Fersman, A. F. Kapustinskii, N. V. Ageev, A. I. Kitaigorodskii, and other scientists.

The work of E. S. Makarov led to formulation of the principle of the structure of "interstitial phases" and to elucidation of the structure of berthollides and daltonides. G. B. Bokii examined processes of ordering in solid solutions, which suggested a crystal-chemical criterion for the composition of an ordered system. B. F. Ormont considered structural and thermodynamic aspects of the chemistry of defective crystals and phases of variable composition, as well as problems of interpreting the physicochemical properties and structure of real crystals.

V. G. Kuznetsov, G. B. Bokii, Z. G. Pinsker studied the crystal structure of semiconducting compounds. A systematic description has been given of the structure of several types of semiconductors.

N. V. Belov showed that a second, diortho-group Si_2O_7 exists in addition to the main Bragg structural unit—the orthosilicate tetrahedron—and that the "configuration" of silicate structures is determined primarily by the cations.

The crystal chemistry of minerals and their synthetic analogues has been developed by E. S. Makarov, V. A. Frank-Kamenetskii, Yu. A. Pyatenko.

Neutron diffraction, the Mössbauer effect, and other methods have been used to investigate double oxides A_2BO_5, and also ferroelectrics, antiferroelectrics, and ferromagnetics. This led to a crystal-chemical theory of ferroelectricity and to a new class of compounds—ferroelectromagnetics (G. S. Zhdanov).

An important branch of crystal chemistry is the study of complex compounds (G. B. Bokii, M. A. Porai-Koshits, G. S. Zhdanov, A. V. Ablov, T. I. Malinovskii, A. I. Kitaigorodskii, and others). The work of crystal chemists made it possible to establish the structure of various types of complexes, interpret their properties, and lay the foundation for theoretical concepts. Systematic structural investigations on compounds of cobalt, nickel, copper, zinc, palladium, and platinum established regularities in exchange of the coordination polyhedron and several peculiarities of the metal–ligand bond (Porai-Koshits).

Chemistry of Complex Compounds

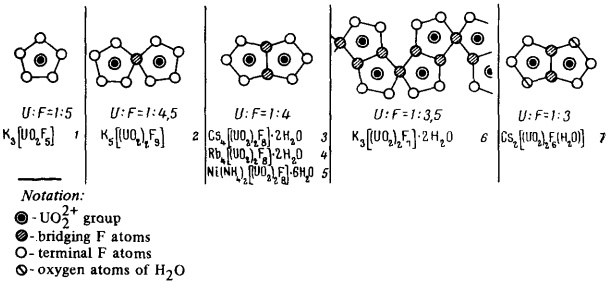
The founder of the chemistry of complex compounds in the Soviet Union was L. A. Chugaev, who discovered several inner-complex compounds of platinum, nickel, and other metals, and established the "rule of rings". The coordination theory of the structure of complex compounds was developed by L. A. Chugaev, I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, B. V. Nekrasov, N. K. Pshenitsin, and many other investigators. Chernyaev's rule of the *trans*-effect of ligands in complexes having a square configuration of the inner sphere underlay the study and preparation of new coordination compounds of platinum, rhodium, palladium, and other noble metals. Grinberg observed also a weaker *cis*-effect of ligands. He based a theory of the acid–base properties of complex compounds on platinum(II) complexes as example.

Several comprehensive investigations have recently been published on the interaction of ligands—a central trend in the chemistry of coordination compounds—revealing finer aspects of the metal–ligand bond. To them may be added an interesting treatment of the *trans*-effect (I. B. Bersuker, A. V. Ablov), K. B. Yatsimirskii's discovery of a kinetic effect in the interaction of ligands and the channels through which it is transmitted in complexes, and the establishment of a model of the *trans*-effect in six-coordinated complexes of transition metals containing a multiple metal–ligand bond (E. M. Shustorovich, Yu. A. Buslaev, M. A. Porai-Koshits).

Dozens of previously unknown complexes of platinum, rhodium, iridium, thorium, uranium, cobalt, nickel, iron, copper, zinc, and other metals have been obtained with various types of ligands containing nitroso-, nitro-, thiocyanato-, cyano-, and sulphato-groups. More than sixty new compounds of uranium and thorium were prepared in 1972 alone.

Developing the chemistry of the actinides, I. I. Chernyaev and R. N. Shchelokov established the law of the replacement of ligands in coordination compounds of uranyl and related complexing groups, which enabled them to prepare many new uranyl compounds. Examination of fluoride complexes of uranyl by X-ray diffraction (Yu. N. Mikhailov) revealed the presence of diverse structural motifs [Table 2].

Table 2.



Procedures based on complex formation have been worked out for separating many valuable metals, e.g. the platinum metals and gold, under both industrial and laboratory conditions. A method has been suggested for isolating copper, silver, and gold by means of sodium tetrahydroborate in the presence of complexing agents from baths used for the deposition of coatings.

Genetic series of complex compounds of uranium, thorium, plutonium, and zirconium have been obtained (I. I. Chernyaev, V. A. Golovnaya, G. V. Ellert, R. N. Shchelokov). Significant differences between complex compounds of radioactive elements and those of platinum metals are evident in the structure of the coordination sphere, the absence of a pronounced *trans*-effect, and a great "affinity" for oxygen-containing, not for nitrogen-containing, ligands. Many compounds predicted by coordination theory have been prepared.

I. V. Tananaev made a systematic study of fluoride and oxofluoride compounds of uranium, plutonium, and thorium, and the higher fluorides of elements of the chromium subgroup, vanadium, and titanium. He developed fluoride processes for the refining of uranium-containing materials.

D. I. Ryabchikov discovered the existence of a large new class of complex compounds of rare-earth metals, whose stability increased with atomic number from lanthanum to lutetium. An important role in the separation of rare-earth metals by the most diverse methods—liquid extraction, ion-exchange chromatography, fractional crystallisation, cathodic reduction—is played by complex formation. A new method of separation—partial complex formation—has been developed. New analytical procedures for rare-earth metals have also been established.

Heteropoly-compounds were investigated by E. A. Nikitina, and inner-complex compounds by S. A. Voznesenskii. A theory that complex formation is amphoteric in character was based on complexes having a non-metallic central atom (Ya. A. Fialkov). The thermodynamic and thermochemical parameters of complexes, used to determine their stability, have been studied by Yatsimirskii.

Direct experimental evidence has been obtained for the existence of stable complex molecules in the gas phase. Equimolecular complexes—$NaBeF_3$, $NaAlF_4$, $NaZrF_5$—and higher complexes—Li_2BeF_4, $(LiAlF_4)_2$, etc.—have been detected.

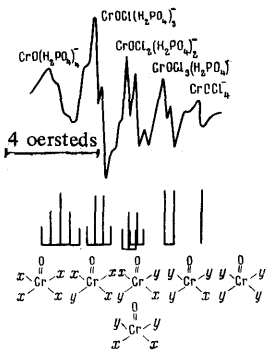


Figure 37. Electron spin resonance spectrum of chromium(V) complexes dissolved in phosphoric and hydrochloric acids.

The application of physical and physicochemical research methods—spectropolarimetry, dielectric measurements, electron spin resonance, nuclear magnetic resonance, etc.—will give valuable information on the structure of complex compounds. K. I. Zamaraev and N. N. Tikhomirova used e.s.r. to investigate the reactions of copper and molybdenum complexes. This method was combined with ultraviolet and infrared spectroscopy to study copper and cobalt complexes. A. N. Ermakov, P. N. Marov, and G. M. Larin are using e.s.r. to study the formation in solution, the nature of the bond, and the structure of coordination compounds of molybdenum(V), chromium(V), cobalt(II), copper(II), vanadium(IV), europium(II), and other paramagnetic ions. Labile *cis*- and *trans*-isomers of coordination compounds of yl ions (oxo-cations) have been discovered in a series of molybdenum(V) and chromium(V) complexes. Fig. 37 illustrates the e.s.r. spectrum of chromium(V) complexes dissolved in phosphoric and hydrochloric acids.

A theoretical model has been constructed for the interaction of ligands attached mainly by σ-bonds to the central atom. The *cis*-effect has been explained for compounds of non-transition elements from a single approach (V. I. Nefedov, Yu. A. Buslaev).

Chemistry of Rare Elements, Semiconducting Compounds, and Materials for Quantum Electronics

It is very important to obtain pure and superpure rare-earth metals, many of which could be separated only after the appearance of nuclear power and the production of their radioactive isotopes. A technology has also been elaborated for the production of pure zirconium, a constructional material for atomic reactors. This problem was one of the most difficult in the chemistry of the rare elements. Methods have been worked out and introduced into industry for obtaining ultrapure tellurium and selenium, necessary for the preparation of semiconductors, rubidium, caesium, beryllium, scandium, and germanium. The chemistry of simple and complex compounds of more than thirty rare elements (halides, oxides, phosphates, chalcogenides, acido-complexes with molecular ligands and with a metal–metal bond) is being studied in the Division of Rare Elements of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences (I. V. Tananaev).

During recent years new applications and new methods of isolation have been found for rare elements. For example, phosphors have been based on lanthanum and ytterbium orthophosphates activated with europium and terbium. Phosphors emitting in a specific region and very durable high-temperature binding materials have been obtained from scandium and gallium phosphates. Several procedures have been worked out for obtaining the spectra of sexivalent rhenium compounds in solution and determining their parameters, which are important for technical processes. New compounds of rhenium have been obtained, as well as polymeric compounds of this metal with heterochains. The problem of producing the ion-exchange resins required for purifying rare elements has been solved. Methods of separation by means of complex formation have been developed.

Many studies are connected with the chemistry of semiconductors. Carbides, silicides, fluorides, and borides of rare elements possess valuable properties. An important trend is the production of ceramet articles and glasses with additions of cerium, neodymium, praseodymium, and other metals.

The chemistry of semiconducting compounds, which has developed during recent decades, forms a separate branch of inorganic chemistry. Solutions have been obtained for the problem of obtaining highly pure germanium (N. P. Sazhin, D. A. Petrov, I. P. Alimarin, I. V. Shmanenkov, and others), silicon (B. A. Sakharov, M. I. Iglitsyn, and others), selenium, and tellurium. Semiconducting properties have been found in grey tin (A. I. Blum, N. A. Goryunova).

Semiconducting binary compounds were obtained by G. G. Urazov, N. A. Goryunova, A. R. Regel', N. P. Luzhna. The types of compounds that are now being prepared and studied are $A^{III}BV$ (BN, AlN, GaP, BP, BAs, InP, etc.), $A^{II}BVI$ (ZnS, ZnSe, ZnTe, CdS, HgS, etc.), $A_2^{III}B_3^{IV}$

(chalcogenides of gallium, indium, and thallium), chalcogenides of rare-earth metals, and many others. Bismuth and antimony chalcogenides are most often used for the production of semiconductors, and arsenic sulphides and selenides for semiconducting glasses. Semiconducting properties have been observed in many oxides (Cu_2O, ZnO, V_2O_5, UO_2, etc.), nitrides, carbides, and silicides of chromium, boron, manganese, iron, etc.

Many more complicated semiconducting compounds—$CuFeS_2$, $AgFeTe_2$, $Cu(Ag)Ge_2P_3$, $Cu_2(Ag_2)SnS_3(Se_3, Te_3)$, etc.—have been prepared and studied during recent years. Several criteria have been suggested for predicting the presence of semiconducting properties in tetrahedral ternary phases (N. A. Goryunova, V. P. Zhuze). Methods used to prepare semiconducting compounds comprise the decomposition of more complicated compounds, chemical transfer reactions, syntheses with counter-pressure, gas-phase reactions, purification by zone melting, etc.

Techniques have been developed for preparing semiconductors having specified properties. Materials have been produced for obtaining filamentous alloyed silicon crystals by gas-diffusion reactions. They have been used as a basis for sensitive miniature strain resistors and temperature and pressure sensors. A new process has been found for obtaining weakly alloyed epitaxial films of gallium arsenide on a strongly alloyed support. A rotating container heated by light has been suggested for growing crystals.

Several semiconducting compounds, e.g. antimony thioiodide, possess both piezoelectric and ferroelectric properties, which makes them promising for use in radioelectronics. Pressure–temperature–composition diagrams have been studied for the antimony(bismuth) iodide—sulphide(selenide) systems, which include the semiconducting ferroelectrics SbSI, BiSI, SbSeI, and BiSeI. Conditions for growing single crystals of these compounds from the gas phase and from the melt have been optimised. Single crystals of considerable size have been obtained with certain of them. Fundamental investigations have been made on complex phosphides and arsenides of the type $A^{II}B^{IV}C_2^V$, which show prospects for semiconductor and laser technology.

Physicochemical methods of analysis are used to obtain "equilibrium microdiagrams" for semiconductors and alloying additives (V. M. Glazov, V. S. Zemskov). These investigations make a considerable contribution to the theory of the alloying of semiconductors. Ternary systems based on antimonides of aluminium, gallium, indium, etc. have been examined. Departures from stoichiometry are under investigation (N. Kh. Abrikosov, M. S. Mirgalovskaya, and others). Physicochemical principles are being elucidated for the preparation of semiconducting materials, based on lead chalcogenides and their solid solutions, with specified properties (A. V. Novoselova and Ya. I. Gerasimov). Procedures have been worked out for the polarographic monitoring of the composition of single crystals with preliminary separation of the elements by ion-exchange chromatography.

Considerable progress has been made in the chemistry of materials for quantum generators and paramagnetic amplifiers. Special methods have been developed for growing crystals (S. A. Peskovetskii) and for producing crystals with a uniform distribution of impurities (S. V. Grum-Grzhimailo), and manufacture of the necessary compounds—the ethyl sulphates of lanthanum, gadolinium, and cerium, corundum (S. K. Popov), fluorite (I. V. Stepanov, B. P. Feofilov), calcium tungstate, etc.—has been set in motion. A search is being made for new materials for quantum electronics, in particular the production of chemical lasers (V. L. Tal'roze), and lasers based on liquid and vitreous media (G. V. Ellert). Methods are being worked out for obtaining ultrapure materials for the microelectronic, semiconductor, and other industries (G. G. Devyatykh).

Radiochemistry

Radiochemistry, which arose after the discovery of radioactivity by Henri Becquerel, began to develop in Russia at the beginning of the twentieth century, mainly in the laboratories of Moscow and St. Petersburg Universities. Study of the radioactive elements and their practical application have been the concern of V. I. Vernadskii, L. S. Kolavrat-Chervinskii, N. N. Beketov, A. P. Sokolov, V. I. Spitsyn, E. S. Bersuker, L. V. Pisarzhevskii, V. A. Borodovskii, K. P. Yakovlev, and many others.

V. G. Khlopin, B. A. Nikitin, A. E. Polesitskii, P. I. Tolmachev, M. A. Pasvik, A. P. Ratner, I. E. Starik investigated the partition of elements between a crystalline phase and a solution, and formulated a rule linking the distribution of trace elements with chemical composition and molecular structure.

Investigations of the distribution of compounds of radioactive elements between two liquid phases and the fundamental problems of extraction are of great practical importance (B. A. Nikitin, V. M. Vdovenko, V. V. Fomin, A. V. Nikolaev, I. P. Alimarin, Yu. A. Zolotov, and others). On the basis of these investigations extraction methods were worked out for the complete and partial separation of the radioelements in lumps of uranium, the isolation of uranium and other elements from industrial wastes, the separation of rare-earth metals, the partition of lanthanides from actinides, etc. Ratner put forward a quantitative theory of adsorption, which is important for separating rare elements on adsorbents and ion exchangers. Studies in this field were made by B. P. Nikol'skii, B. N. Laskorin, A. M. Trofimov, V. I. Paramonova.

Aspects of the qualitative and quantitative analysis of mixtures of rare-earth metals by ion exchange and complex formation, partition and paper chromatography, have been investigated by A. P. Vinogradov, D. I. Ryabchikov, K. V. Chmutov, A. K. Lavrukhina, and others. Significant results were obtained by A. D. Gel'man on the separation of transuranium elements—neptunium, plutonium, americium—by means of complexing agents. Starik examined the state of a substance under conditions of extreme dilution.

Radiochemical analysis—the separation, identification, purification, and quantitative determination of radioisotopes in natural specimens, irradiated targets, etc.—is very important in present-day radiochemistry. The analytical principles were worked out by Vinogradov, Khlopin, Polesitskii, Starik. Methods for the radiochemical analysis of the fission products of heavy nuclei and isotopes formed by the action of neutron and other types of irradiation have been elaborated by B. V. Kurchatov, Yu. M. Tolmachev, V. P. Shvedov, and others.

The establishment of nuclear reactors and accelerators led to the synthesis of new elements—from neptunium to element 107. G. N. Flerov was the first to synthesise elements having atomic numbers 104 and 105. Methods were worked out for isolating elements 106 and 107 from the products of the action of accelerated xenon ions, and for their identification.

Hitherto unknown isotopes and compounds have been obtained. The existence of californium, einsteinium, and fermium in the bivalent state has been discovered. V. I. Spitsyn, N. B. Mikheev, together with scientists at the Joint Institute for Nuclear Research (in the town of Dubna), obtained univalent mendelevium for the first time, the first element to be obtained in this state of oxidation, which is abnormal for actinides. An. N. Nesmeyanov developed a technique and regulations for obtaining technetium (No. 95) from a niobium and molybdenum target that had been exposed in a cyclotron, by extraction with an aliphatic ketone from sulphate solutions containing small quantities of fluoride and nitrate ions. B. F. Myasoedov developed a chromatographic method of ultrapurification from contamination with californium, providing a source of neutrons for small-scale equipment.

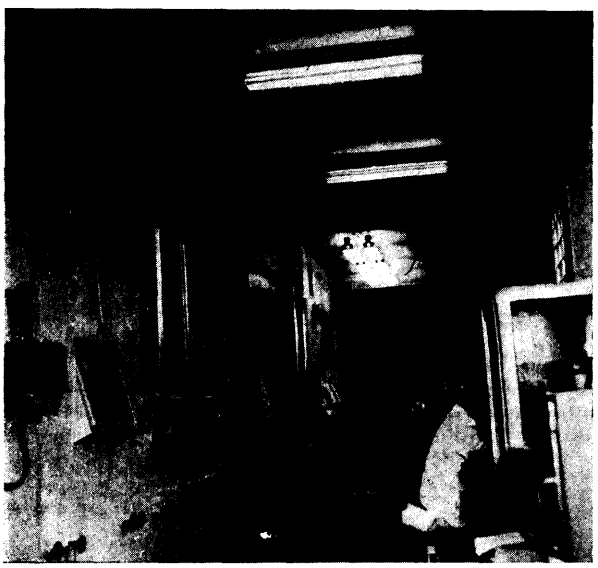


Figure 38. "Hot chambers" for work with highly radioactive substances (Institute of Physical Chemistry of the USSR Academy of Sciences).

Lavrukhina designed and constructed assemblies of low-background radiometric units permitting the examination of minute quantities of radioactive isotopes (down to 1 disintegration min^{-1} kg^{-1}) in large quantities of material (up to 1 kg). A method was proposed for determining subatmospheric dimensions of meteorites by radiochemical analysis of radioactive isotopes. A series of researches has been completed on the radiochemical analysis of the content of the cosmogenic isotopes—aluminium-26 and sodium-22—in a lunar regolith supplied by the automatic station Luna-16.

Great attention is being paid to the contamination of the environment with radioactive materials, the burial of wastes, the estimation of radioactivity in the vicinity of atomic installations, and problems of dosimetry (Spitsyn). An investigation of the behaviour in sea-water of fission products from a nuclear fuel (plutonium-239, ruthenium-106, technetium-99, cobalt-60, manganese-54, etc.) has been completed by V. V. Gromov. Study of the behaviour of radioactive isotopes and elements during their bioassimilation by phytoplankton under natural conditions in the South-eastern region of the Pacific Ocean has shown that radioactive fission products are efficiently assimilated and concentrated by the phytoplankton within 1–2 days. This promotes rapid transmission of the fission products of a nuclear fuel along the biological chain.

phytoplankton → zooplankton → fishes → man

which is a further justification for demanding a ban on the dumping of fission products in the ocean.

Almost all radioactive and stable isotopes—cobalt-60, caesium-137, strontium-90, phosphorus-32, iodine-131, boron-10, nitrogen-15, carbon-13, etc.—are now produced in the Soviet Union.

Chemistry of Natural Salts

The Soviet Union occupies the leading position in the world with respect to reserves, richness, and variety of composition of natural salts and brines.

Physical chemists and chemical hydrologists have made laboratory and field investigations of salt lakes in various regions of our country—the Crimea, Western and Eastern Siberia, the Caspian Depression, etc.—in which an important part was played by N. S. Kurnakov, V. I. Nikolaev, V. P. Il'inskii, S. Z. Makarov, B. L. Ronkin, I. N. Lepeshkov, M. G. Valyashko, Yu. P. Nikol'skaya, A. V. Nikolaev, and many others. New mineral salts were discovered, industrial methods for extracting salts were developed, and the salt equilibria in the lakes were studied, which contributed to optimising technical processes for the isolation of salts from natural brines.

In order to establish the genesis of the natural salts, systematic investigations were made of the solubility and other properties of complicated systems containing sulphates, hydrogen carbonates, carbonates, chlorides, and other salts. The results provided a justification for existing methods or led to new technical processes for obtaining salts from natural brines. S. I. Vol'fkovich worked out a process for converting mirabilite into sodium carbonate and ammonium sulphate—a valuable nitrogen fertiliser.

Investigations of great value for the national economy were made on potassium–magnesium deposits in the Solikamsk District, the Ural, Carpathian and Volga salt beds, where deposits having an increased potassium content and minerals containing boron were discovered, the potash beds of the Hissar Ridge and Tyubeg-tan in Uzbekistan, gameto-glauberitic deposits on the Tyan'-Shan in Kirgizia, deposits of epsomite, common salt, and gypsum in the Uzboi river bed in Turkmenia, and sylvinite–carnallite deposits at Starobino in Belorussia.

Phosphate beds have been investigated, and methods developed for enriching them and converting them into fertilisers, phosphorus, phosphoric acids, and other products (E. V. Britske, S. I. Vol'fkovich, A. I. Shereshevskii, N. N. Postnikov, M. L. Chepelevetskii, N. S. Kurnakov, A. G. Bergman, M. I. Ravich, L. G. Berg, F. M. Perel'man, A. B. Bekturov, M. N. Nabiev, M. E. Pozin, and many others). Thanks to these investigations the Soviet Union is able, not only to avoid importing phosphate minerals, but also to export its production to other countries.

The phase constitution, solubility, and thermal decomposition of natural carbonates and sulphates formed by the evaporation of sea-water have been examined. (These

compounds are used in water installations and for the production of building materials, plastics, and heat-insulating materials.) Ravich showed that salts that are almost insoluble in water under normal conditions become soluble at high temperatures (up to 600°C) and water-vapour pressures (up to 2500 atm). Problems involved in an optimal technology for processing natural deposits are being solved.

Great attention is being paid to detecting rare and trace elements, and isolating them from the salt ores. Thermographic, microthermal, and high-speed thermographic methods of analysis have been developed for this purpose, together with dilatometric phase analysis.

The chemistry of silicates is the basis of many important industries—cement, glass, ceramics, refractories, etc. Its task is to study methods for the preparation of silicate materials and their properties, as well as the processes occurring in them during operation. Silicate chemistry directly related to the technology of silicate manufacture has been the concern of N. V. Belov, P. A. Rebinder, P. P. Budnikov, N. A. Toropov, and many others.

Studies have been made on the structure of cement, the relation between its properties and mineralogical composition, the effect of mineralisers on processes of exchange, the processes involved in firing, and setting. Causes of the corrosion of cements have been elucidated, and measures developed for combating it (A. A. Baikov, S. I. Druzhinin, B. S. Shvetsov, and others). Technical processes have been worked out for obtaining special types of cement by the use of new types of raw material and industrial wastes, activators, surface-active additives, plasticisers, etc. The setting of cements at high temperatures and pressures has been investigated in connection with the production of ferroconcrete, polymer cement, etc. articles (M. M. Sychev, V. I. Korneev, V. N. Yung, V. A. Kind, B. V. Volkonskii, P. F. Konovalov, S. D. Makashev, V. B. Ratinov, O. P. Mchedlov-Petrosyan, S. I. Druzhinin, B. S. Shvetsov, I. L. Znachko-Yavorskii, A. P. Kreshkov, and many others).

Research has been undertaken on the chemistry of glass (D. S. Rozhdestvenskii, N. N. Kachalov, I. V. Grebenshchikov, G. Yu. Zhukovskii, A. A. Lebedeva, I. I. Kitaigorodskii, M. A. Bezborodov, M. A. Matveev). The technology of quartz glass has been developed by M. S. Maksimenko. Studies have been made to improve industrial processes and find ways of producing glass with special properties, glass–enamel refractory coatings, organosilicate materials, etc.

Recent decades have seen the establishment of a new branch of chemical science—the chemistry of the solid state—which studies chemical processes involving solid phases, determines the relation between the reactivity of solids and structural features, and elaborates a general theory of the controlled formation of solid compounds with the aim of producing effective new materials for present-day technology.

ANALYTICAL CHEMISTRY

Research on analytical chemistry in the Academy of Sciences originated with M. V. Lomonosov, who established the principles of quantitative chemical analysis and made numerous analyses of salts, minerals, and ores. Great contributions to the development of analytical chemistry were subsequently made by T. E. Lovits, V. M. Severgin, G. I. Gess [Hess], F. F. Beil'shtein [Beilstein].

During the early years of the Soviet State development began of a theory and new methods of analytical chemistry, especially those involved in solving applied problems of importance for the national economy. L. V. Pisarzhevskii, N. A. Tananaev, I. P. Alimarin, A. K. Babko, A. M. Dymov, and many others assisted in studying the natural resources of the country. Research was undertaken on the composition of rocks and minerals, as well as the contents of rare elements in various natural materials, and standard methods of analysis were developed for heavy chemical industry, metallurgical processes, ores, and useful fossils (V. I. Vernadskii, K. A. Nenadkevich, I. D. Borneman-Starynkevich, and others). Directly related investigations were made on the degree of purity of chemical compounds and the preparation of pure chemical reagents (V. V. Longinov, E. S. Przheval'skii, A. V. Rakovskii, A. E. Uspenskii).

Problems connected with developing chemical and physical methods of controlling the production of radium, uranium, and vanadium, separating them, and concentrating them were solved under the direction of V. G. Khlopin.

During the 1920–1930s analytical methods were developed for controlling production in works laboratories and for rapid analysis (N. A. Tananaev, A. M. Dymov, E. S. Przheval'skii, V. D. Voznesenskii, F. K. Gerke, I. P. Alimarin, A. M. Zan'ko, I. V. Tananaev, G. S. Landsberg, and others). Colorimetric, spectral, electrometric, and other methods of analysis became widely used. Great attention was paid also to standardising analytical methods.

The need to determine impurities in reagents and small quantities of rare elements in natural materials led to the appearance during the 1920s of special new, highly sensitive methods, including spot tests. A non-destructive method of analysis was developed for metals and alloys, as well as a fractional method of analysis (N. A. Tananaev).

Analysis by examining crystals under the microscope, established long ago by Lovits, was further developed. L. A. Chugaev, V. G. Khlopin, O. E. Zvyagintsev used a colorimetric method to analyse metals of the platinum group. Nikol'skii developed a method of potentiometric titration, and subsequently the theory of the glass electrode. Establishment of the first polarographic laboratories in our country is associated with the names of V. I. Vernadskii and A. P. Vinogradov. Internal electrolysis was established by Yu. Yu. Lur'e and Yu. A. Chernikhov, a sedimentometric method by N. A. Figurovskii, and a new form of volumetric analysis, vanadatometry, by V. S. Syrokomskii. The classic methods of analysis—gravimetric, titrimetric (A. K. Babko, I. V. Tananaev, I. P. Alimarin, I. M. Korenman, A. I. Busev, R. P. Lastovskii, and others)—have not lost their value. In the field of photometric analysis much attention has been paid to studying the mechanism of colour reactions, the processes of complex formation in solution. New reagents have been produced for the qualitative and quantitative determination and separation of almost all elements (V. I. Kuznetsov, N. S. Poluektov, S. V. Savvin, A. M. Lukin, and others).

Theoretical principles underlying the present search for new highly sensitive reagents have been established by L. M. Kul'berg (principle of functionally analytical and analytically active groups, and of the role of the nature of the metal) and by Kuznetsov (problems of the appearance of colour, use of the intramolecular dissociation of cyclic salts, mechanism of reactions with organic precipitants, etc.). N. P. Komar' studied the photometry of multicomponent mixtures, and K. B. Yatsimirskii developed a kinetic method of analysis. The luminescence method of

analysis established by S. I. Vavilov has been developed by M. E. Konstantinova-Shlezinger, E. A. Bozhevol'nov, D. P. Shcherbov, A. V. Karyakin, and others.

Spectral emission analysis is widely used to analyse metals, alloys, ores, and high-purity materials (D. S. Rozhdestvenskii, S. E. Frish, V. K. Prokof'ev, S. A. Borovik, A. N. Filippov, G. S. Lansberg, B. A. Lomakin, A. K. Rusanov). A rapid and accurate method of flame photometry has been developed by Poluektov. Studies by N. I. Tarasevich, V. V. Nedler, A. N. Zaidel' have been concerned with methods for the spectral analysis of ultrapure substances. A theory of emission spectroscopy has been elaborated during recent years, and processes occurring at the electrodes have been studied, as well as the mechanism of the vaporisation of material, excitation in the gas phase, etc. New modifications of the method are applied, in particular with the use of lasers. X-Ray spectral analysis has been developed by I. B. Borovskii, M. A. Blokhin, N. P. Il'in, N. F. Losev, Ya. E. Vainshtein This method is successfully applied to the analysis of metals, alloys, minerals, cements, and slags, as well as for phase analysis.

Polarography is widely used by A. M. Dymov, T. A. Kryukova, V. F. Toropova, I. P. Alimarin, S. B. Tsfasman. The theory of amalgam polarography is due to A. G. Stromberg; with accumulation on the mercury drop this method has been developed by S. I. Sinyakova, E. N. Vinogradova, A. G. Stromberg. Amperometric titration is widely used by I. P. Alimarin, O. A. Songina, Yu. I. Usatenko, V. A. Khadeev, and others. Potentiometric titration was further developed by N. A. Izmailov and then by A. P. Kreshkov, especially in non-aqueous media. High-frequency titration (V. A. Zarinskii) is used for the analytical control of production.

A promising and accurate coulometric method of titration has been used by M. S. Zakhar'evskii, A. Ogarev, F. I. Grishin. Several theoretical methods in the field of coulometry have been developed by P. K. Agasyan, who has studied the interrelationship among the various electrochemical methods.

Gas analysis forms a separate branch of analytical chemistry. Gas analysers of various types, in particular photocolorimetric, have been produced. Determination of the content of gases in metals, which is extremely important for the metallurgical industries, began to be developed by N. P. Chizhevskii, P. S. Lebedev, Yu. A. Klyachko, Z. M. Turovtseva.

Gas-chromatographic analysis, which is widely employed at the present time both for analytical and preparative purposes in scientific research and for the control of production, is sensitive, accurate, and simple. Such methods have been developed by A. A. Zhukhovitskii and N. M. Turkel'taub, who have elaborated new forms—chromathermography, a dynamic thermal method, vacancy chromatography, stepwise chromatography, chromatography without a carrier gas. V. G. Berezkin has studied the application of gas chromatography to analytical chemistry.

Mass spectroscopy is used to analyse solids—pure substances, semiconductors, materials for nuclear technology. V. L. Tal'roze has developed a method combining chromatography and mass spectrometry (chromatographic mass spectrometry).

The development of radiochemistry and the atomic industry provided the opportunity for new radiochemical methods of analysis. Radioactivation analysis has been widely used by I. P. Alimarin and Yu. V. Yakovlev. Natural radioisotopes came to be utilised as indicators. Analytical methods have been based also on the scattering or the absorption of β- or γ-rays. X-Radiometry, isotopic dilution, and radiometric titration have also been developed.

Optical methods of analysis have been widely used. Refractometry has been elaborated by B. V. Ioffe, and spectropolarimetry is successfully applied by A. P. Terent'ev, V. M. Potapov, E. G. Rukhadze.

Special types of analysis—micro and ultramicro—utilise various chemical and physicochemical techniques. Ultramicroanalysis involving use of a microscope has been developed by I. P. Alimarin and M. N. Petrikova. These lines of attack have been applied to the analysis of minerals and ores in geochemistry.

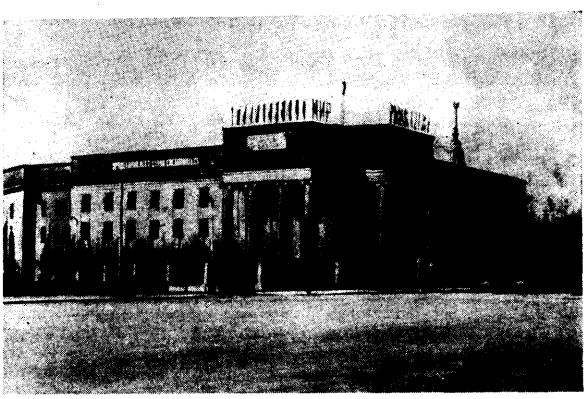


Figure 39. Vernadskii Institute of Geochemistry and Analytical Chemistry.

The problem of the analysis and control of production of atomic materials in our country has been successfully solved (A. P. Vinogradov, P. N. Palei, D. I. Ryabchikov, B. P. Nikol'skii, I. P. Alimarin, I. E. Starik, I. V. Tananaev). The efforts of a group of scientists of the USSR Academy of Sciences and of branch scientific research institutes (I. P. Alimarin, N. P. Sazhin, Yu. A. Zolotov, M. S. Chupakhin, Yu. V. Yakovlev, A. V. Karyakin, Z. M. Turovtseva, L. L. Kupin) have been concentrated on solving the problem of obtaining and analysing pure materials (high-purity metals, semiconducting materials, and chemical reagents).

A considerable contribution to the development of the analytical chemistry of rare elements and rare-earth metals has been made by A. P. Vinogradov, I. P. Alimarin, D. N. Ryabchikov, A. N. Ermakov, M. M. Senyavin, A. I. Ponomareva, and others.

The wide use of synthetic and natural organic compounds in industry and scientific research has stimulated the development of new methods of organic analysis. Important studies are being made in several institutes of the USSR Academy of Sciences on the elementary and functional analysis of organic substances using physical and physicochemical methods (A. P. Terent'eva, M. O. Korshun, V. A. Klimova, N. E. Gel'man).

The wide range of facilities of modern analytical chemistry has been applied in examining materials from the lunar surface procured by Soviet automatic stations.

Unique data have been obtained on the composition and structure of lunar rocks, the significance of which it is difficult to overestimate.

The growth of science and technology presents analytical chemistry with new problems—to enhance accuracy and sensitivity, accelerate the analysis, evolve methods of local analysis and remote analysis, and to automate analytical control.

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Within the confines of a single paper, of course, it is impossible to cover all lines of chemical research, even in general form. For this reason there may have been omissions of names, which is especially unfortunate both intrinsically and because the Reviewer feels the deepest respect for his scientific colleagues both of the past and of the present day. Nevertheless, the hope should be expressed that this outline will reinstate in the reader's memory the glorious historic road travelled by chemistry in our country, and recall the herculean, selfless, and enthusiastic labours, filled with romance, of many generations of Russian chemists.

The USSR Academy of Sciences, in celebrating its 250th anniversary, can be justly proud of the names of its illustrious scientific chemists, who over the ages have glorified Russian chemical science.

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