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Chemistry in the USSR

N.M.Emanuel'

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I. INTRODUCTION

As the science of substances, materials, and products which meets a wide variety of humanity's requirements, chemistry has played an important role in all the stages of the development of the Soviet State.

In pre-revolutionary Russia only isolated scientific schools were active and there existed an extremely weakly developed chemical industry. It was therefore only as a result of the activities of talented scientists such as Lomonosov, the founder of chemical science, and subsequently Mendeleev and Butlerov, that Russian chemists were able to maintain a high reputation of Russian chemistry in world science.

The Soviet epoch in the life of our Motherland, which has been in general characterised by exceptionally high rates of scientific and technical progress, became for chemistry also a period of the flowering of fundamental research and the construction of a powerful modern chemical industry. It is generally known that at the present time the USSR occupies the first place in the world in the manufacture of mineral fertilisers and the second place in the total volume of chemical production.

Large scientific schools arose, numerous chemical research institutes as well as specialised higher and intermediate scientific establishments have been created, there has been an unusual increase in the number of research chemists, professors, and lecturers with the highest qualifications, and membership of the large army of industrial chemists—workers and mechanics in chemical combines and undertakings, engineers and technicians, and workers in branch institutes and factory laboratories—has become an honoured status.

In the Academy of Sciences of the USSR and the Academy of Sciences of the Union Republic alone there are more than 50 chemical institutes. Chemical research in hundreds of research institutes of the Ministries of the chemical, petroleum processing and petrochemical, mineral fertiliser, and cellulose and paper industries, as well as the institutes of many other Ministries, Departments, and higher educational establishments is being prosecuted in close collaboration with the above institutes.

The form of the chemical laboratories, which have now been placed in buildings specially constructed for them, has been completely altered. The experimental methods of modern physics, radioelectronics, computer technology, and

experimental design and automation have been widely introduced into research practice.

Chemistry in our country embraces an exceptionally wide range of the most important fundamental and applied problems. The coordination of scientific research, which has been called upon to ensure effective interrelated work of the institutes of the Academy of Sciences of the USSR, the Academies of Sciences of the Union Republics, chemical industrial establishments, and higher educational establishments, as well as the Chemical Sections of the Academies of Sciences of socialist countries within the framework of the existing plans of multilateral and bilateral collaboration, has therefore become important. The Academy of Sciences of the USSR has been successfully fulfilling its role as the coordinator of all scientific research in our country in full conformity with the resolutions of the Party and Government of our Motherland. This work is being achieved, in particular, as a result of the activity of the extensive network of councils on scientific problems in various branches of chemistry, whose members include outstanding representatives of chemical science regardless of the particular departments to which they belong. The conferences of Academician-Secretaries of the Chemical Sections of the USSR Academy of Sciences and the Academies of Sciences of Union Republics with participation of the responsible representatives of the Ministries and Departments, held in Baku (1976) and Tbilisi (1980), have played a definite role in combining the efforts of chemists towards the solution of the most urgent problems of chemical science and practice. A conference of the Academician-Secretaries of the Chemical Sections of the Academies of Sciences of socialist countries, devoted to the same purposes, was held in Moscow in 1980.

Soviet chemists have taken an active part in all the most important international undertakings, in the first place those under the aegis of the International Union of Pure and Applied Chemistry (IUPAC). The scientific and technical relations with the chemical establishments of many capitalist countries, particularly as regards problems such as those of catalysis, polymer chemistry, petrochemistry, the kinetics and mechanisms of chemical reactions, and physiologically active and medicinal preparations, have been expanded.

L.I.Brezhnev's words "... without a modern large-scale chemistry there can be no effective economics", spoken at the October (1980) Plenum of the Central Committee of the Communist Party of the Soviet Union, have been exceptionally inspiring for all chemists of our country.

The role of science in the solution of the key problems of the national economy in the eleventh five-year plan was exceptionally highly assessed in L.I.Brezhnev's report to the XXVIth Congress of the Communist Party of the Soviet Union. Soviet chemists have therefore devoted enormous attention to specific combined scientific and technological programmes concerning the manufacture of polymeric materials, the development of the small-scale chemical industrial production, the development of plant protecting agents, the creation of highly efficient catalysts, the synthesis of new inorganic materials, the synthesis of artificial liquid fuel, the development of chemical means of extracting petroleum from geological strata, and other urgent problems.

The aim of the present review is to attempt a description of the overall pattern of development of the main trends in the chemical science in the USSR, including the proceedings of the annual meetings of the Division of General and Technical Chemistry of the USSR Academy of Sciences during the last decade.

Evidently, within the framework of a journal article, it is virtually impossible to carry out such a task, because the limited space makes it impossible even to describe simply the scientific profiles of the numerous chemical establishments let alone mention the names of all chemists who merit this having brought glory to Soviet chemistry as a result of their selfless labour. At the same time, one would wish to think that this review will remind readers of certain stages on the road traversed by Soviet chemists during the years of the existence of the USSR.

II. PHYSICAL CHEMISTRY

1. Quantum Chemistry and the Theory of Molecular Structure

Quantum chemistry, which in the USSR is the concern of more than 100 research groups, constitutes the theoretical foundations of modern chemical science. A comprehensive collaboration of scientists from the Socialist countries on the problem of "quantum chemistry" has been organised since 1979. The participation of Soviet specialists in the work of the Committee of Experts on Quantum Chemistry organised on the initiative of UNESCO in France has been activated.

Quantum-chemical research methods have been converted into an effective instrument for the investigation of the structures and reactivities of molecules. Computer calculations of the electronic structures and properties of molecules have been widely carried out with the aid of these methods. Much attention has been devoted to quantum-chemical studies in the electronic theory of condensed systems and materials science, the investigation of elementary atom–molecule processes, the development of the quantum theory of surface phenomena, adsorption, catalysis, and electrochemical processes, the development of a theory of magnetic and spin effects, and the application of quantum-chemical approaches to problems of biology and pharmacology and to the solution of problems of the specific synthesis of chemical compounds ("computer synthesis").

The development of quantum-chemical studies has become possible by virtue of the large-scale introduction of modern methods of theoretical physics, the improvement of computational methods, and the employment of high-class computers. The All-Union Information Centre for Quantum-Chemical Computational Programmes (the Institute of Organic Chemistry of the USSR Academy of Sciences, the Institute of General Chemistry) and a specialised library of quantum-chemical programmes (Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences, Siberian Division of the Institute of Chemical Kinetics and Combustion) have been created. More than 100 programmes are being used nowadays for non-empirical and semi-empirical calculations on molecular systems (Yu.N.Molin and P.V.Schastnev).

A definite contribution has been made to the creation of a system of data banks on the structures of chemical compounds. A system of information search for the solution of structural problems by molecular spectroscopic methods has been developed at the Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences (V.A.Koptyug) together with the Computer Centre of the Siberian Division of the USSR Academy of Sciences. The system is based on the application of modern computers and a library of spectroscopic information, in which virtually all published atlases, catalogues, and files on molecular spectroscopy are collected (the library contains at the present time more than 90000 infrared spectra, approximately

30000 ultraviolet spectra, and 25000 ^{1}H NMR spectra of chemical compounds).

The combination of the development of the theory of structure and of the science of reactions of compounds with the results of experimental studies has been traditional for chemical science.

Fundamental research has been carried out on the theory of magnetic relaxation. The theory of saturation in NMR, based on the concept of the spin–spin temperature, developed by B.N.Provotorov, has received recognition. Theoretical studies have stimulated the development of new experimental fields in the study of structure and the transformations of matter with the aid of nuclear magnetic resonance. The results obtained in this connection have served as a basis for the interpretation of multipulse high-resolution NMR spectra, which made it possible, in particular, to establish the nature of the molecular movement in crystalline hydrates. The theory of relaxation processes, based on the method of random trajectories, has been developed. It permitted the investigation of the molecular movements in various media, for example, the molecular movements under the conditions of high viscosity were investigated for the first time (N.N.Korst).

P.P.Shorygin discovered and interpreted a new phenomenon—resonance Raman light scattering (RRS), which led to the development of a new branch of molecular spectroscopy. The fundamental characteristics of the resonance Raman scattering on pulsed irradiation were investigated and new possibilities of this method in chemistry were established. A single quantum theory of the resonance and non-resonance Raman light scattering has been developed. It makes it possible to determine the form of the excited electronic states of simple molecules from the intensity and frequency dependence of the resonance Raman spectra and indicates the possibility of a new phenomenon—the light-induced conformational transformation of polyatomic molecules of a specific class (S.I.Vetchinkin).

The theories of molecular spectra, vibrational-rotational interaction (M.A.El'yashevich), and vibrational spectra (M.A.El'yashevich and M.V.Vol'kenshtein), are being developed. Methods permitting the extraction of the necessary information from spectoscopic data have been worked out.

Quantum-chemical calculations have been performed on magnetic interactions in molecules and radicals, in particular those adsorbed on the surfaces of solids; a theory whereby EPR and NMR data can be related to molecular structure has been developed (G.M.Zhidomirov and P.V.Schastnev).

The foundations of the quantum theory of the hydrogen bond have been laid. A theory of the infrared spectra of crystals with hydrogen bond chains has been developed and a multiphonon model of the vibrational spectra of solutions of acids and bases with strong hydrogen bonds has been proposed. The dynamic theory of molecular hydrogen-bonded complexes and charge-transfer complexes made it possible to explain from a single standpoint the characteristics of the geometry and infrared spectra of these compounds (N.D.Sokolov).

Soviet investigations into the theory of elementary atom–molecule processes occupy an important place in world science. A theory of the non-equilibrium decomposition of diatomic molecules has been developed. A general theory of the redistribution of energy among the active degrees of freedom of the molecule, incorporating the earlier theories of unimolecular decomposition as special cases, has been created. A statistical theory of bimolecular reactions proceeding via the formation of a long-lived complex has been established (E.E.Nikitin).

A theory of the unimolecular decomposition of a one-component gas at high temperatures under the conditions of non-equilibrium population of the vibrational levels, when the vibrational relaxation time is comparable to the time of an elementary chemical step, has been developed (N.V.Kuznetsov).

The classical methods for calculations on reactions involving the tunnel transfer of a hydrogen atom explained the experimentally observed rates of reactions between radicals and hydrocarbons at low temperatures (M.Ya.Ovchinnikova).

A theory of vibrational-rotational relaxation has been created taking into account the resonance transitions in molecular collisions (A.I.Osipov).

A general theory of elementary chemical processes, in particular the charge transfer process in the liquid phase taking into account the involvement of the medium in the chemical reaction step, has been proposed. The conditions for the consecutive and synchronous transfer of two electrons in a polar liquid have been elucidated (I.V.Aleksandrov). A quantitative theory of the rates of energy and charge transfer as a function of the translational and rotational mobility of the reactants has been developed (A.I.Burshtein).

A theory of the influence of the magnetic field on the rates of radical chemical reactions has been created and the dependence of the magnetic resonance spectra on the nature of the movement and the interaction of the radical pairs (RIMMR spectra) has been developed (S.I.Kubarev).

A quantum-mechanical theory of collective donor–acceptor interactions, characteristic of a large class of new substances (organic metals), has been created. The vibrational relaxation times of large molecules in the condensed phase have been calculated and the possibility of the existence of long-lived vibrational states was predicted and subsequently confirmed experimentally (A.A.Ovchinnikov).

A quantum-mechanical model of the low-temperature polymerisation in molecular crystals has been proposed (M.V.Bazilevskii).

Advances have been made in the quantum-mechanical description and experimental study of the elementary step in electrochemical reactions in relation to metallic electrodes coated by insulating or semiconducting films. Conditions have been determined under which one of two different reaction mechanisms predominates, namely tunnelling or electron transfer via band states in a film (R.R.Dogonadze, A.M.Kuznetsov, and L.I.Krishtalik). A quantum theory of proton transfer in polar liquids has been developed (R.R.Dogonadze, A.M.Kuznetsov, A.A.Ovchinnikov, M.Ya.Ovchinnikova, and I.V.Aleksandrov).

A theory of the oxidation-reduction reactions in a polar liquid has been set up and used successfully to explain the absolute rates of heterogeneous electrochemical reactions involving electron transfer from the metal to the electrolyte (A.A.Ovchinnikov).

As early as 1950s–1960s, Ya.K.Syrkin and M.E.Dyatkina made a significant contribution to the theory of the electronic structure of chemical compounds and developed ideas concerning the involvement of unshared electron pairs and vacant orbitals in chemical bonding, put forward the concept of the effective atomic charge, and examined problems of chemical reactivity. These studies exerted a notable influence on the development of the quantum chemistry of inorganic compounds.

In subsequent years a series of non-empirical calculations of the electronic structures of compounds of light elements, the kinetics of chemical processes in the atmosphere, and the composition and thermodynamic functions of vapours over thermostable coatings were carried out; calculations were

also made in other instances where direct experiments are difficult (O.P.Charkin).

A theory has been proposed and computer calculations have been made for the structures of non-rigid molecules which made it possible to eliminate the existing fundamental contradictions between the results of spectroscopic and electron diffraction methods concerning the structures of non-rigid molecules containing boron (N.F.Stepanov).

Studies have been published on the nature of vibronic interactions, the spectroscopic manifestations of the Jahn–Teller effect, dipole instability, and the characteristics of the chemical properties of molecular systems in degenerate and quasi-degenerate electronic states, which are important for the chemistry of coordination compounds. Numerous calculations of the structures of organic and coordination compounds have been made (I.B.Bersuker).

The mechanisms of thermal and photochemical isomerisations have been established and the relative stabilities of the *cis–trans*-isomers of the complexes of a series of metals have been explained on the basis of quantum-chemical calculations (A.A.Levin).

The stability of hexavalent curium, confirmed by experiments on the β-decomposition of $^{252}_{95}Am(V)$, has been predicted (V.I.Spitsyn and G.V.Ionova).

The dependence of the physicochemical properties of inorganic compounds on the asymmetry of the valence and vacant orbitals has been investigated, which made it possible to account for the characteristics of the behaviour of molecules containing atoms with *f* electrons (K.B.Yatsimirskii).

Quantum-mechanical calculations have been made on chemical bonds and a detailed description of the distribution of atoms and vacancies in many inorganic compounds and their solid solutions has been achieved (V.A.Gubanov).

A significant contribution has been made to the theory of the electronic structure and properties of organic compounds. A theory of the correlation interactions in organic polymers has been developed, which made it possible to predict the existence of organic ferromagnetic materials (A.A.Ovchinnikov).

A method has been developed for the analysis of the properties of the wave functions of molecular systems on the basis of the concept of the entropy of quantum-chemical distributions. New qualitative methods have been proposed for the investigation of the electronic structure of molecules on the basis of topological approaches; new mathematical models have been put forward for the description of organo-elemental systems of the sandwich type (D.A.Bochvar).

The steric structures of cyclo- and bicyclo-propyl ethers, selenides, α-aminoethers with the nitrogen atom in different states of hybridisation, and aromatic and acetylenic sulphides and selenides have been determined (B.A.Arbuzov, A.N.Vereshchagin, A.V.Il'yasov, and R.R.Shagidullin).

The structures of the frontal orbitals of unsaturated compounds containing polar substituents have been determined and their reactivities have been characterised; the effect of the interaction of polar groups with π orbitals has been estimated (Yu.P.Kitaev and V.V.Zvered).

The characteristics of the solutions of the self-consistent field equations for molecules with a low energy of the singlet–triplet transition, which explain the nature of the biradical states of cyclic hydrocarbons, have been investigated (M.M.Mestechkin).

It has been shown by quantum-chemical methods that the reaction of ethylene with anions can proceed via two different mechanisms as a function of the mutual orientation of the reactants (Yu.L.Frolov).

The properties of phosphazo-compounds—their ability to undergo one-electron reduction oxidation, complex formation, and dimerisation—have been interpreted quantum-mechanically as a function of the nature of the substituent and the geometry and electronic structure of the compound (G.G.Dyadyusha, Yu.N.Nezel'skii, and V.V.Pan'kovskii).

The stability of clathrate compounds of organic molecules with the inert gases has been estimated and their geometry has been established (A.B.Bolotin).

An artificial intellect system has been created on the basis of a computer for the automatic identification of organic and organoelemental compounds with up to 40 atoms from infrared, Raman, ultraviolet, NMR, and mass spectra by

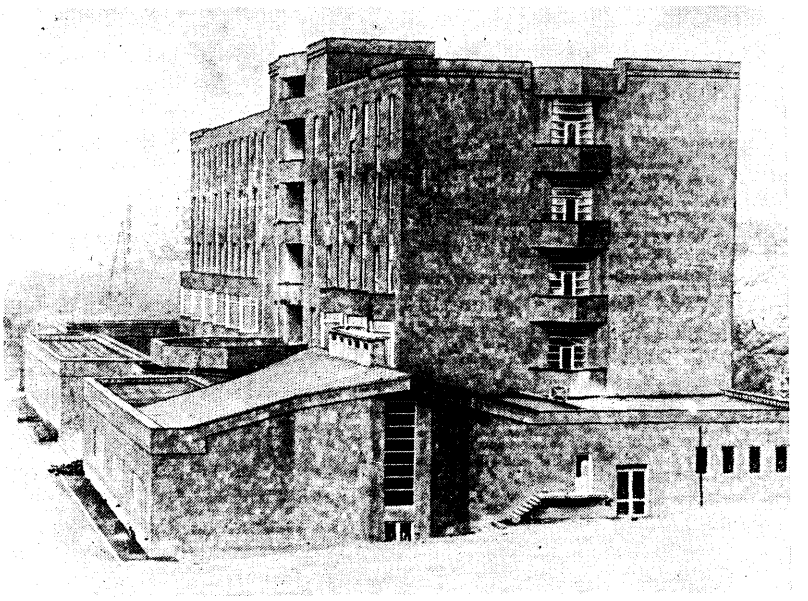


Figure 1. Institute of Chemical Physics of the Academy of Sciences of the Armenian SSR.

comparing spectroscopic data with the results of quantum-chemical calculations (L.A.Gribov).

Quantum-chemical methods are widely used in studies of the properties of the surfaces of solids and the structure of crystals and in the determination of the mechanisms of heterogeneous catalysis.

A new method has been developed for the calculation of the electronic structures of perfect and defective crystals on the basis of an improved cluster model, which is particularly important for the development of a theory of adsorption (R.A.Evarestov).

Quantum-chemical calculations have been made on the principal types of active centres on the surfaces of heterogeneous catalysts and on the kinetics of catalytic reactions involving such centres. It has been shown that chemical interaction with a Lewis acid centre should entail a significant alteration of its geometry. The low reactivity of the silicon atom as the coordination centre in chemisorptive processes in systems of the type of aluminosilicates has been demonstrated (V.B.Kazanskii, G.M.Zhidomirov, and I.M.Mikheikin).

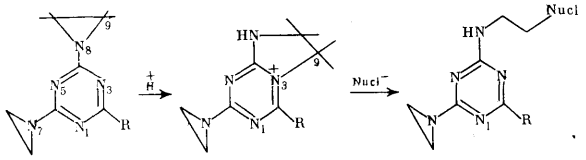
A new field of quantum chemistry, related directly to problems of physicochemical biology, is developing. The relation between the structures and biological activities of these compounds has been analysed with the aid of quantum-chemical methods for the calculation of the structures of certain biologically active compounds.

The electronic structures of 2,2,6,6-tetramethyl-4-X-piperidine *N*-oxide [X = H, OH, =O, $(CH_2)NH_2$, OCONHPh, $OCONH_2$, or NHCON ◁] have been calculated by the INDO method.

The influence of the local molecular environment and of the nature of the substituent X on the redox properties of nitroxy-radicals has been estimated. The electronic charges on the atoms, the spin densities, the electrostatic potential of the space around $R^{\cdot}$, the energies of the unoccupied and occupied molecular orbitals, and the difference between the total energies of $R^{\cdot}$ and R^{-} have been calculated for these radicals ($R^{\cdot}$) and their reduced forms (R^{-}). The structures of the hydrate complexes of R and R^{-} have been investigated. Comparison of polarographic data with the results of calculations for certain radicals showed that the oxidation potential of R^{-} can be described in terms of the values of $E_3(R^{-})$.

The calculated values have been compared with acute toxicity data (LD_{50}) for five different radicals $R^{\cdot}$. The existence of a reliable relation between LD_{50} and $E_3(R^{-})$ has been demonstrated: the enhancement of the electron-accepting properties of $R^{\cdot}$ leads to a decrease of toxicity. The oxidation reactions of the reduced forms of $R^{\cdot}$ proceeding with formation of $O_2^{\cdot-}$ and not the $R^{\cdot}$ reduction reactions are probably responsible for the toxicity of the nitroxy-radicals (V.B.Luzhkov).

The electronic structures of the cyclic intermediates in nucleophilic substitution reactions of 4,6-diaziridino-*sym*-triazines have been calculated:



The stabilisation energy of the intermediate is proportional to the electrostatic component of the total energy:

$$E_{N,C} \propto Q_N Q_C / r_{NC} .$$

The calculated [subject to the condition $r_{N(3)C(9)}$ = const.] values of $f_{NC} = 10^4 \times Q_{N(3)} Q_{C(9)}$ for the intermediate with different substituents R were compared with the antitumour effect *P* (percentage of cured animals) (V.G.Kartsev and A.S.Nabatov). Fig.2 illustrates the dependence of *P* on f_{NC}, which permits the prediction of the antitumour activities of other preparations of this kind. This approach can be extended also to other classes of antitumour compounds with an alkylating mechanism of action and containing nucleophilic centres.

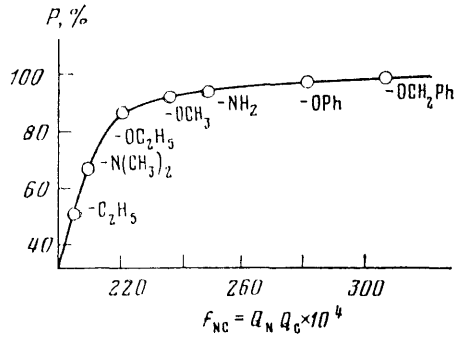


Figure 2. The Coulombic energy of the stabilisation of the carbonium ions derived from substituted diaziridino-triazines and their biological activity (antitumour properties).

2. Physical Methods for the Investigation of Molecular Structure

The structures and conformations of molecules, complexes, and radicals have also been studied experimentally using the entire arsenal of modern physical and physicochemical methods, which has become available in recent years in the laboratories of many institutes. Modern instruments consist of combinations of optical spectrometers, microwave spectrometers, mass spectrometers, etc. with a computer, which permits (particularly under the conditions of full automation) a rapid interpretation and storage of the information obtained and also the determination of the optimum conditions for the experiments.

X-Ray diffraction analysis is one of the fundamental methods for the study of the molecular structures of single crystals, polycrystalline substances, liquids, gases, and individual molecules. The elucidation of the tertiary steric structures of proteins may be regarded as the main achievement of X-ray diffraction analysis (V.K.Vainshtein and Yu.A.Ovchinnikov).

Fig.3*a* illustrates the structure of leghaemoglobin of *Lupinus luteus* (molecular weight 17000)—an oxygen-binding protein present in the nitrogen-fixation system of plants and having the α-helical structure.

The structure of catalase from *Penicillium vitale*—a protein with a molecular weight of ~280000 and consisting of four subunits whose function is the decomposition of hydrogen peroxide—has been determined. The structure of the subunit is shown in Fig.3*b*. Evidently each subunit has a complex structure and consists of three domains (A, B, and C) of different structure. The active domain C has the most complex structure, based on the cylindrical packing of eight polypeptide chains in the β-configuration surrounded by α-helices. The B domain is purely α-helical, while both the A and C domains have a configuration of the α + β type. The last two domains have apparently a regulating function.

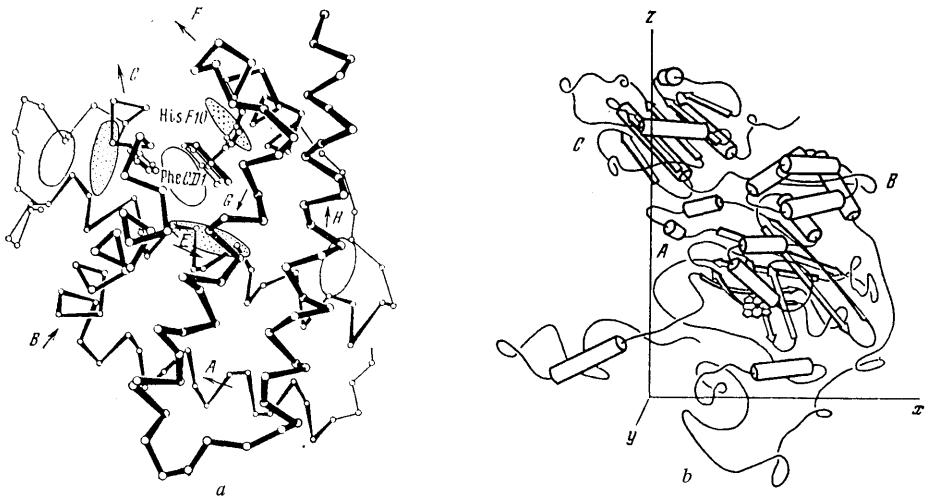


Figure 3. *a*) The structure of the polypeptide chain in the leghaemoglobin molecule. The α-carbon atoms and the functionally important aminoacid residues Phe CD 7 and His F 10 near the active centre are shown; *b*) the domain structure of the subunit of the catalase molecule. Cylinders—α-helices; flat arrows—β-chains.

Complex computer systems have been developed for the solution of structural problems. An automatic DAR-1 diffractometer has been devised (D.M.Kheiker). The coupling of an automatic diffractometer with a "Dnepr" controlling computer has been achieved and the appropriate programmes have been devised. The communication channel between this system and the central computer complex (with a "large" computer) has been developed by L.O.Atovmyan. The combined diffractometer–computer system makes it possible to reduce the duration of the experiment by a factor of 10–20.

A qualitative advance in X-ray diffraction studies has been due to the employment of synchronous radiation generators (lasers) as sources and also the creation of new detectors of the diffracted radiation. This permitted the study of the dynamics of the changes in the structure of the given object. The structural changes in muscle during its contraction have been studied by G.M.Frank and A.A.Vazina; the time taken to obtain consecutive X-ray diffraction patterns was several milliseconds—the so-called "cine-diffraction" method.

Powerful synchronous radiation is used in X-ray spectroscopic studies. The EXAFS method, suitable for the determination of certain structural characteristics of substances—the distances to the nearest atoms, small changes in these distances in processes, and the coordination numbers in the environment of the atom chosen for investigation—has been particularly developed. The first studies were carried out at the Institutes of the Siberian Division of the USSR Academy of Sciences (I.A.Ovsyannikova, K.I.Zamaraev, and R.Z.Sagdeev).

A new high-temperature gas electron diffraction method, used for the investigation of the structures of inorganic molecules at temperatures up to 2500 °C, has been developed. These studies were initiated in the USSR. Theoretical foundations have been formulated for the study of the structures of molecules in a high-temperature vapour using the diffraction pattern based on the scattering of fast electrons, apparatus permitting the investigation of substances up to 2500 °C has been created, and methods have been developed for the recording and interpretation of electron diffraction patterns at high temperatures. The structures of substances belonging to the principal classes of inorganic compounds have been investigated (P.A.Akishin, V.P.Spiridonov, E.S.Zasorin, N.G.Rambidi, and Yu.S.Ezhov).

It has been suggested that complex conformational equilibria be analysed by the combination of the Rayleigh light scattering method, double refraction in an electric field (the Kerr effect), and dielectric measurements (B.A.Arbuzov and A.N.Vereshchagin).

A novel mass-spectrometric method for the determination of the structures and compositions of polymers on bombardment of the latter by neutral atoms has been developed. This made it possible to extend the methodological possibilities of mass spectrometry in the region hitherto inaccessible to this procedure—relatively involatile molecular substances. In the new method the target made of the polymeric material is bombarded by accelerated neutral atoms and the charged particles dislodged from the target by them are analysed with the aid of the mass spectrometer. During such bombardment, large charged fragments, containing up to 10 and more atoms and carrying quantitative information about the composition and structure of the polymer, are displaced from the polymer. It has thus been possible to overcome the difficulties associated with the search for a method whereby solids can be ionised without loss of information about their structure and composition (V.L.Tal'roze and G.D.Tantsyrev).

The methods of optical molecular spectroscopy occupy an important place in studies of the structures and compositions of compounds and their reactivities. Soviet scientists have made a large contribution to the creation and development of research methods such as Raman spectroscopy (L.I.Mandel'shtam and G.S.Landsberg), photoelectron

spectroscopy (A.N.Terenin and F.M.Vilesov), infrared absorption spectroscopy of substances in the adsorbed state (A.N.Terenin), the resonance Raman spectroscopy (P.P.Shorygin), and measurement of absorption and emission spectra in paraffin matrices (E.V.Shvol'skii).

Optical spectroscopic methods have recently developed further, particularly in connection with the employment of lasers as radiation sources, which expanded the possibilities of the existing methods and led to the appearance of a multiplicity of new methods with unique possibilities for the investigation of the structure and composition of matter.

Investigations of the spectra of crystals, polymers, fibres, and inorganic and organometallic compounds are developing. Low-temperature spectroscopy constitutes a new method for the study of the spectra of liquid cryosolutions, which, together with the existing methods of matrix spectroscopy, permits the investigation of the formation of weak complexes. Such complexes have been studied for the olefin–halogen, metallocene–halogen, etc. systems (G.B.Sergeev).

The high power of laser sources (energy density up to 10^{16} W cm^{-2}) made it possible to devise a series of new nonlinear methods and their resonance variance based on the phenomena of hyper-Raman light scattering, inverse Raman light scattering, coherent anti-Stokes Raman light scattering (CALS), the Kerr effect induced by Raman light scattering, etc. Some of these have been used in chemical research, particularly the CALS method. The high resolution characteristic of this method made it possible to measure the rotational-vibrational structure of Raman spectra with a high degree of resolution and to obtain hitherto inaccessible information, for example, about the structure of the Q-branches of vibrations prohibited in infrared absorption (V.V.Smirnov and I.L.Fabelinskii). Combination with the method of diode infrared spectroscopy, also characterised by an exceptionally high resolution, made it possible to obtain results which are essential for the development of a theory of molecular spectra with a higher degree of accuracy than before (M.R.Aliev). A variant of CALS method—active polarisation Raman spectroscopy—makes it possible to study the structure of the Raman line within the limits of its homogeneous width and to isolate in certain cases the antisymmetric component of the Raman-transition tensor, which is significant when electronic excitation is involved in the Raman light scattering (S.A.Akhmanov).

The study of the resonance transitions in the excited states in the electronic absorption and Raman spectra has become possible. The relevant data have now been obtained for many molecules both organic and inorganic.

A new field of study involving the investigation of Raman spectra at the electronic levels has developed. Data concerning the fine spectral structures of certain π-complexes of *d*-series transition metals with unclosed electronic shells have been obtained by this method (V.T.Aleksanyan).

The possibility of the localisation of the excitation of the spectrum on illumination by a laser of a small section of the specimen (whose size is of the order of magnitude of the exciting radiation wavelength) led to the creation of new research methods which have been called "sterically resolved spectroscopy". These methods make it possible to study the topology of the distribution of the substance in a long specimen. The sterically-resolved spectroscopic technique is used to study polymeric and biological materials, in mineralogy, and in the semiconductor industry. This technique has also been applied in the investigation of flame topography, in studies under extreme conditions (at high pressures, at low and ultralow temperatures, in the investigation of processes occurring on catalysts, on electrodes, etc.). Furthermore, the technique is used for the determination of impurities in the atmosphere at a distance with the aid of specially designed apparatus (L.P.Malyavkin).

A new phenomenon—the enhancement of Raman scattering for molecules adsorbed on the surfaces of certain metals, namely the giant Raman effect—was discovered several years ago; the enhancement is by a factor of 10^5–10^6. The nature of this effect has not so far been fully elucidated but presumably it will have promising applications in catalytic chemistry and electrochemistry.

Polarisation of laser radiation also made it possible to devise a series of new methods for the investigation of molecular structures. These include studies on circular dichroism in infrared and Raman spectra due to the non-zero values of the derivatives of the components of the optical activity tensor with respect to the normal coordinate of optically active molecules. The information obtained with the aid of these methods is much more complete than that derived in the study of the circular dichroism in electronic absorption spectra.

New possibilities have arisen for the investigation of molecular dynamic processes in the condensed state. Here one uses the possibility of the separate measurement of the isotropic and anisotropic Raman scattering, which makes it possible to obtain information about the characteristics of the vibrational and reorientation relaxation of molecules. Studies in this field are prosecuted in combination with direct measurements of the vibrational de-excitation (T_1) and vibrational dephasing (T_2) times by picosecond Raman spectroscopic methods and are based on a theory which has been developed in detail (A.I.Burshtein). The data obtained in such investigations are important not only for the understanding of the nature of the condensed state but also, for example, for the investigation of chemical kinetics (V.E.Pogorelov).

The possibility of the formation of ultrashort high-power pulses with the aid of modern lasers led to the development of picosecond spectroscopy, whereby one can investigate photophysical and photochemical processes which occur in the picosecond and subpicosecond ranges and which are inaccessible to other research methods. The solution of one of the most important problems in chemistry, involving the study of the evolution of systems from an initial energy distribution and geometry to a final state via different intermediate states, has become possible. Apart from the excitation dissipation processes in the gas phase, various processes in the condensed state are widely investigated nowadays—the rates of the singlet–singlet and triplet–triplet transfer of excitation (using luminescence spectra), the reorientation movement of molecules in a liquid, solvation processes, intramolecular proton transfer, and other processes important for chemistry. Studies of the vibrational relaxation of excited electronic states using "hot" luminescence spectra are of interest (K.K.Rebane).

Considerable advances have been made in the picosecond spectroscopic studies of biologically important processes, for example, the mechanism of night vision and the luminescence of haemoglobin and its complexes. Much has been done to elucidate the mechanism of the transfer of excitation energy from antenna pigments to the active centres of photosynthesising units, where photosynthesis takes place (S.A.Akhmanov).

Spectroscopic methods are being developed in which the excitation sources are X-ray and electron emitters—photoelectron, X-ray electronic, and Auger spectroscopy. These methods, based on the recording of the absorption of radiation as a result of the ionisation of inner and valence levels

in molecules, yield valuable information about the electronic structures of the molecules (Yu.G.Borodko).

A method has been developed for the measurement of the optical diffuse reflection spectra of oxide catalysts in the near infrared. Its advantages relative to transmission spectra are illustrated in Fig.4. Evidently, the reflection spectrum (Fig.4*a*) contains more information than the transmission spectrum of a thin disc pressed from a mixture of powders of amorphous aluminosilicate and silica gel (Fig.4*b*). The absorption lines of the combination frequencies of the stretching deformation vibrations as well as the overtones of the stretching vibrations in the transmission spectrum are almost unresolved. On the other hand, the quality of the reflection spectrum is not inferior over the entire spectral range to that in the main region.

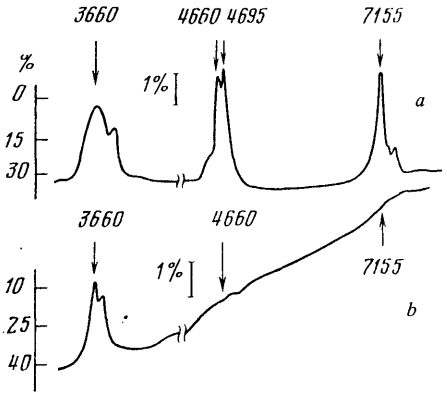


Figure 4. Optical diffuse reflection (*a*) and transmission (*b*) near infrared spectra of a thin disc of an oxide catalyst.

The infrared spectra of the hydroxy-groups in the hydrogen-forms of X and Y zeolites have been investigated by this method and it has been shown that the zeolites do not contain two types of OH groups, as has come to be assumed, but at least three different types of hydroxy-groups. Their infrared spectra are resolved only in the region of the combination frequencies of the stretching and deformation vibrations, which is readily accessible for the diffuse reflection method but cannot be investigated by the usual method involving the recording of transmission spectra (V.B.Kazanskii).

The electron paramagnetic method, discovered in 1944 by E.K.Zavoiskii and widely introduced into chemical research by V.V.Voevodskii, is an extremely effective physical method. Fundamental problems in chemical kinetics and reactivity of free radicals and atoms have been studied experimentally and solved with its aid. New versions of the EPR method, greatly extending its scope, have been developed in recent years.

The method of the optical detection of EPR spectra has been widely used to detect short-lived radical pairs in solution. A spectrometer with the highest recording sensitivity, which makes it possible to measure the EPR spectrum with a resolved hyperfine structure at an average concentration of radical pairs of approximately 100 spins in the specimen and having a lifetime down to 10^{-8} s, has been constructed. The method is applicable in those cases where the recombination of radicals is accompanied by chemiluminescence. An example of such a reaction is the recombination of the aromatic ions A^- and A^+ formed by ionising radiation. The initial radical pair exists in this case in the singlet state; its recombination gives rise to an excited singlet molecule which emits light. The EPR spectrometer is tuned to be in resonance with one of the electron spins of the pair, the orientation of the spin is altered, and the pair then passes to the triplet state. The recombination product is an excited triplet molecule which does not luminesce in solution. Thus the EPR absorption is detected from the decrease of the luminescence signal, which can be done with an extremely high sensitivity.

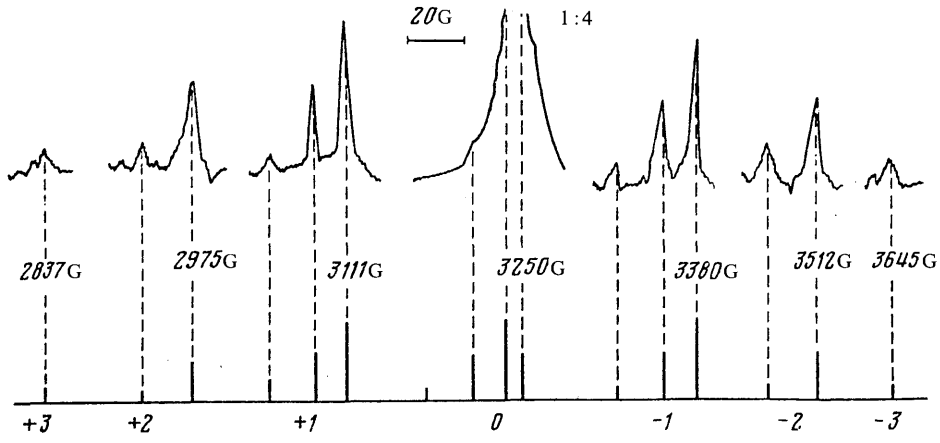


Figure 5. Optically detectable EPR spectrum of the $C_6F_6^-$ ions.

Fig.5 presents the optically recorded EPR spectrum of the negative ion $C_6F_6^-$. The high resolution of the method made it possible to observe in each binomial component of the hyperfine structure a secondary splitting associated with higher-order interactions. The spectrum is satisfactorily described by the theory. At the centre of the spectrum there is an unresolved intense line of the second partner of the pair—the anthracene cation. The spectrum has been obtained at an average concentration of approximately 100 radical pairs in the specimen with a lifetime of 10^{-7} s.

By virtue of its high sensitivity, the method proposed can lead to new possibilities for the investigation of reactions of short-lived radical pairs in reactions of different types. For example, the EPR spectra of the radical-ion pairs (naphthalene)$^-$/(naphthalene)$^+$, (biphenyl)$^-$/(biphenyl)$^+$, and (hexafluorobenzene)$^-$/(anthracene)$^+$, arising on exposure of solutions of the corresponding substances in squalane to ionising radiation, have been recorded (Yu.M.Molin).

A set of methods for the investigation of magnetic resonance in the submillimetre region of the spectrum (from 2 to 0.01 mm), which have no analogues, have been created. Fig.6 illustrates the efficiency of the submillimetre magnetic resonance method in the elucidation of the structure of a biradical molecule. The volume of information extractable from .he EPR spectrum in the 2-mm region is much greater than in the case of the "usual" spectrum in the centimetre range and is sufficient for an unambiguous determination of the steric molecular structure.

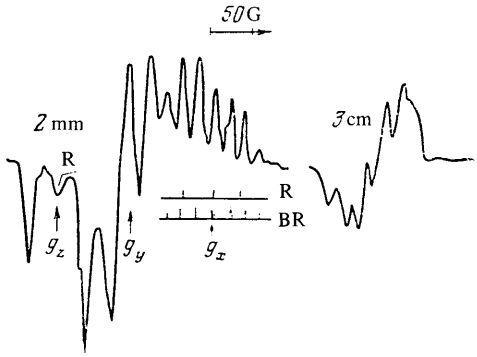


Figure 6. EPR spectra of the *trans*-bis(1-hydroxy-2,2',5,5'-tetramethyl-3-oxo-3-imidazolin-4-yl)ethylene radical in the 2-mm and 3-cm ranges.

A magnetic spectrometer based on a discretely retunable laser with optical pumping (in the range 0.1–0.7 mm), permitting the detection of free radicals in the gas phase with a sensitivity exceeding by several orders of magnitude that of the EPR method, has been developed (Ya.S.Lebedev).

The use of the NMR parameters in the analysis of structural data made it possible to determine the coordinates of hydrogen atoms and the atoms of elements adjoining hydrogen in the Periodic System and having similar X-ray scattering factors. An algorithm and a set of computer programmes have been developed whereby the broad-line NMR method can be used to confirm the correctness of the structural model and to find the most probable structure.

3. Automation and Computer Technology in Chemical Research

A set of computer programmes of the "Flamingo" type has been set up for synthetic organic chemistry. It is designed for the determination of the possible ways of synthesising specific compounds and is based on a formal logical approach to the solution of structural problems in organic chemistry. The aim of the programmes is single-stage determination of all possible processes with cyclic electron transfer in closed chemical systems, taking into account specified limitations. Problems associated with the homology and "isomorphous substitution" in organic structures have been solved and problems of tautomerism and the molecular design of organic reactions in closed systems have been considered. For example, the ways in which the skeleton of tricyclo[2,1,0,$0^{2,5}$]. .pentane can be constructed have been calculated. Computer calculation made it possible to reproduce the familiar synthetic approaches to derivatives of this tricyclic system and to discover new reactions (including an unusual degenerate rearrangement) which merit experimental study (Fig.7) (N.S.Zefirov).

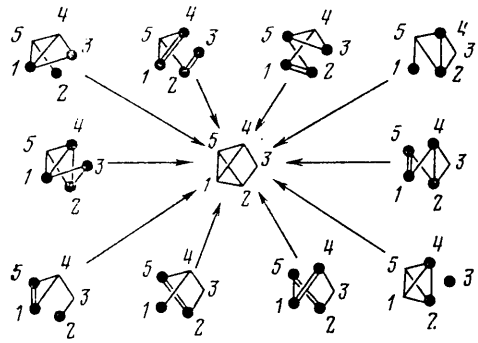


Figure 7. The most promising methods of synthesis of tricyclo[2,1,0,$0^{2,5}$]pentane found with the aid of a computer.

An important scientific field involving the application of computer technology to chemical research, namely macromolecular chemistry, is being developed. Computer calculations are used to simulate and solve converse problems in polymer chemistry. Models of processes in which the polymer chain is formed from small fragments have been constructed on the basis of the formalism of finite Markov chains. The problems of the construction of models of chemical reactions of macromolecules are being solved by the Monte Carlo method.

The scope of mathematical modelling in specific polymeric systems has been demonstrated in relation to the benzylation of poly-4-vinylpyridine. The converse problem has been solved with the aid of kinetic experimental data, namely the individual kinetic constants, which are in the ratios 1:0.3:0.3, have been estimated. These values have been used to model by the Monte Carlo method the functions governing the composition distribution of the three copolymers which are the reaction products. The composition inhomogeneity was studied simultaneously by the gel chromatographic method. The results of the calculation are compared in Fig.8 (continuous lines) with the results of the experimental study.

The rotational isomeric lattice model of the micro-Brownian movement of the polymer chain and an intramolecular cross-linking reaction have been developed. When a number of limitations, corresponding to the real conditions in the formation of chemical cross-links in solutions of low viscosity are observed, it is possible to calculate the kinetics of the process, which is autocatalytic owing to the decrease of the volume of the coils and of the concentration of the cross-linking groups on cross-linking.

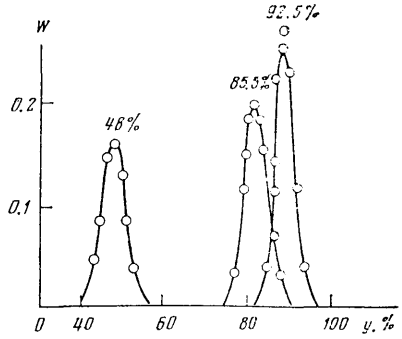


Figure 8. The composition distribution in the benzylation products of poly-4-vinyl-pyridine; continuous lines—calculated results; circles—experimental data.

A set of programmes for the solution of converse problems in the theory of the neighbour effect, including problems of the minimisation of the sum of squares of deviations and of the determination of the dependence of the error of the estimates obtained on the experimental error, are being developed. This permits a correct experimental design and a comparison of the theoretical models with the experimental results.

Many problems can be solved successfully on micro-computers. A system of programmes for the analysis of poorly resolved NMR spectra of polymers and the dialogue method have been proposed for execution on large computers and minicomputers (N.A.Plate).

4. Chemical Kinetics

Chemical kinetics—the science of the chemical process, its mechanism, and the characteristics of its time course—is one of the most important branches of chemical physics. The systematic study of the rates of chemical reactions was begun by N.A.Menshutkin as early as the end of the past century. The establishment and development of this field are closely associated with the names of Russian and Soviet scientists. Among the first studies of the mechanisms and kinetics of complex oxidation reactions were those of A.N.Bakh and N.A.Shilov.

Much attention has been devoted to the investigation of the kinetics and mechanisms of chemical reactions in the gas phase, but subsequently the kinetic research included again a wide variety of chemical reactions occurring in the liquid phase and in solutions and recently also solid-phase reactions (including those at ultra-low temperatures) and the processes in biological systems.

Reactions in the gas phase. A major achievement of Soviet science in chemical kinetics has been the theory of branched chain reactions created in the 1930s by Academician N.N.Semenov and his school. As early as 1926, N.N.Semenov, Yu.B.Khariton, Z.S.Val'ta, and A.I.Shal'nikov discovered new phenomena which did not fit within the framework of the existing ideas concerning the mechanisms of chemical reactions. In the oxidation of phosphorus vapour they observed instances of sharp transitions from almost complete inertness to the inflammation of the mixture (after the attainment of a critical oxygen pressure or a critical size of the reaction vessel). These studies constituted the basis of the theory of branched chain reactions, which became exceptionally widely known.

Numerous phenomena characteristic of branched chain processes were investigated, namely the existence of the lower and upper inflammation limits, the unusual form of the regions of the chain inflammation of combustible gases in the form of "peninsulas" on pressure–temperature plots, the characteristics of the effect of inert gases and vessel size on the lower inflammation limit, and the influence of active impurities and the walls of the reaction vessel.

Limiting phenomena were also observed in the oxidation of gaseous sulphur, hydrogen, carbon monoxide, carbon disulphide, ethane, phosphine, arsine, silane, and hydrogen sulphide. Many of the chain inflammation processes investigated indicated a wide occurrence of branched chain reactions (A.V.Zagulin, A.A.Koval'skii, P.Ya.Sadovnikov, I.D.Kopp, F.I.Dubovitskii, A.B.Nalbandyan, N.M.Chirkov, V.V.Voevodskii, Yu.N.Ryabinin, and P.S.Shantorovich). Most attention has been devoted over a period of many years to the kinetic study of the hydrogen oxidation reaction (this reaction can be regarded as the classical model of a branched chain process).

Numerous studies designed to provide an experimental justification of the chain theory have been carried out. Thus A.A.Trifonov showed in classical experiments that the rate of an unbranched chain reaction involving the photochemical formation of hydrogen chloride from hydrogen and chlorine decreases with decrease of the vessel diameter (owing to chain termination on the walls). They also found that, with increase of pressure, the difference between the rates is smoothed out, since an increased pressure increases the length of the path traversed by the active centres on their way to the walls.

Unbranched chain processes, which have been included in chemical kinetic investigations as a result of the studies by M.Bodenstein and W.Nernst, were examined from new points of view, which arose as a result of an intense development of the theory of branched chain reactions. Theories of chain termination on the walls and in the space within the reaction vessel were created for both types of chain processes and the general case of chain termination both in space and on the surface was examined theoretically (V.R.Bursian and V.S.Sorokin). Differential equations on their integral forms were obtained for unbranched and branched reactions whereby chain propagation as a function of time, i.e. the kinetics of such processes, could be described (N.N.Semenov).

The studies by A.A.Koval'skii, N.M.Chirkov, P.Ya.Sadovnikov, M.B.Neiman, A.I.Serbinov, B.V.Aivazov, V.A.Shushunov, and M.F.Pushlenkov on the slow oxidation reactions of the simplest hydrocarbons in the gas phase (methane, ethane, propane, and pentane) were important for the subsequent development of the field of chain reactions. These studies must be regarded as the experimental justification of N.N.Semenov's theory of the slow propagation of an avalanche-type chain reaction, i.e. slowly developing non-stationary processes—the so-called chain reactions with

"degenerate" branching ("degenerate explosion"). The theory of these processes makes it possible to understand and describe quantitatively many instances of the slow development of the chain avalanche, which does not lead to the inflammation of the combustible gas mixture.

Extensive experimental data of foreign investigators, whose studies of both the chemical systems already mentioned and a number of others (oxidation of benzene, ethylene, and acetylene, low-temperature oxidation of aldehydes, oxidation of a sodium sulphite solution, thermal decomposition of oxygen compounds of chlorine, thermal decomposition and explosion of ozone, and photochemical decomposition of nitrogen trichloride and solutions of hydrogen peroxide) were analysed from the standpoint of the general theory of chain reactions.

N.N.Semenov's fundamental monograph "chain reactions" (1934), which surveys the results of studies of chain reactions and establishes the canonical features of chemical reactions of this type, gained world renown.

One of the main conclusions of the theory of branched chain reactions is that high concentrations of free radicals are formed in branched chain processes. As early as the end of the 1930s and the beginning of the 1940s, numerous studies were carried out to determine the concentrations of free radicals in chain reactions. Methods were developed whereby one could investigate free atoms and radicals as active centres of chain reactions: the linear absorption method (V.N.Kondrat'ev, L.I.Avramenko, and M.S.Ziskin) and the catalytic probe method (V.N.Kondrat'ev and E.N.Kondrat'eva). Hydrogen atoms and OH and COS radicals were detected in the combustion reactions of H_2 and CS_2. The formation of SO free radicals in the slow oxidation of H_2S was also established (N.N.Semenov, D.S.Pavlov, and N.M.Emanuel'). In all cases the concentration of the free-radical species in the branched chain processes exceeded by many orders of magnitude the values corresponding to thermodynamic equilibrium.

The application of physical research methods, whereby it is possible to identify the active centres in chain reactons, to investigate the elementary processes involving them, and to measure the rate constants for these processes, have come to play an increasingly important role in the determination of the mechanisms of chain reactions.

In his early studies V.N.Kondrat'ev already applied the electron impact method to the investigation of the dissociaton of species and was the first to employ mass spectrometry to study chemical reactions. Later the mass-spectrometric method was developed in the investigations of V.L.Tal'roze. The diffusion cloud method in a stream was devised for the investigation of the reactions of atoms with molecules in the gas phase in order to determine their rate constants (V.L.Tal'roze).

The EPR method has been used successfully in the study of the kinetics and mechanisms of gas-phase reactions. A.B.Nalbandyan observed the formation of large amounts of H and O atoms and OH radicals in the combustion reaction of hydrogen, of SO radicals in the oxidation of hydrogen sulphide, and of many free radicals in other reactions.

N.N.Semenov and V.V.Azatyan found that the content of Cl atoms in the NCl_3 flame at room temperature reaches 40% relative to the amount of the initial substance. The formation of P atoms in the classical phosphorus vapour oxidation reaction was noted (V.V.Azatyan).

The new highly sensitive laser magnetic resonance (LMR) method was employed recently to investigate the mechanisms of branched chain oxidation and chlorination reactions of silane. High concentrations (up to 10^{13} cm^{-3}) of $SiH_3^{\cdot}$ radicals and Cl atoms were detected (Fig.9) by the laser magnetic resonance method in the region of these reactions (V.N.Panfilov).

Chain reactions involving interaction between the chains have been studied in relation to many examples (N.N.Semenov and V.G.Voronkov). N.N.Semenov and V.V.Azatyan examined at a new level of physical experiments and computer technology in relation to many examples of classical branched chain gas-phase reactions the problem of the necessity to take into account non-linear chain termination reactions both in space and on the surface, arising as a consequence of high concentrations of active centres. This made it possible to describe more rigorously and correctly the kinetics of branched chain processes in the gas phase.

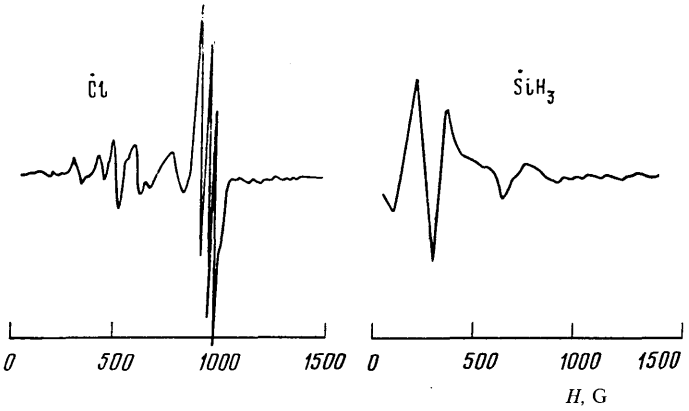


Figure 9. Laser magnetic resonance spectra of the chlorine atom and the $SiH_3^{\cdot}$ radical in the products of the reaction of SiH_4 with Cl_2.

N.N.Semenov's scientific achievements in the study of the mechanisms of chemical reactions were recognised in 1956 by the Award of the Nobel Prize in Chemistry.

The kinetics and mechanism of the methane oxidation reaction have been investigated (A.B.Nalbandyan, N.S.Enikolopov, A.M.Markevich, N.A.Kleimenov, and L.V.Karmilova). This reaction was considered as one of the possible ways of manufacturing formaldehyde. Much attention has been devoted to the determination of the chemical mechanism of the chain oxidation reaction of propane (V.Ya.Shtern and S.S.Polyak).

A new phenomenon involving a macroscopic multistage mechanism of a complex chain process, where intermediate products are formed in the initiating stage and are then responsible for the selective oxidation of propane to acetone, was discovered in the study of the oxidation of propane in the presence of hydrogen bromide. The process can be controlled by acting on each macroscopic stage separately. These studies initiated a cycle of investigations of homogeneous catalysis in gas-phase chain reactions. A macroscopic multistage mechanism was also established in the oxidation of aldehydes in the gas phase. An unusual behaviour of the intermediate hydroperoxides, ensuring under certain conditions an explosive course of the process, was observed (N.M.Emanuel', E.A.Blyumberg, Z.K.Maizus, T.E.Pavlovskaya, G.Ya.Timofeeva, V.M.Cherednichenko, D.G.Knorre, and R.F.Vasil'ev).

The phenomenon of the heterogeneous branching of homogeneous chains in the gas-phase low-temperature degenerately branched oxidation reactions of organic substances (acetaldehyde and propionaldehyde) has been observed. It was established that the rate of the heterogeneous radical decomposition of the intermediate peracids HCO_3H, CH_3CO_3H, and $C_2H_5CO_3H$ (as well as H_2O_2 and hydroperoxides) depends to a large extent on the nature and character of the treatment of the surface of the reactor (A.B.Nalbandyan).

In connection with the study of the role of the surface in chain reactions, one should mention that as early as 1927 M.V.Polyakov suggested the possibility of heterogeneous chain initiation. In 1948 A.A.Koval'skii showed with the aid of his method, involving separate calorimetric measurements, that many catalytic reactions beginning on the surface of the catalyst are continued in the gas phase and obey a chain mechanism (homogeneous-heterogeneous reactions).

N.N.Semenov suggested the possibility of the formation of free radicals in steps involving bimolecular interaction between saturated molecules. Experimental proof of this was obtained by A.E.Shilov and F.S.D'yachkovskii in relation to the interaction of triphenylmethyl chloride with ethyl-lithium.

Among kinetic studies having a long history, mention should be made of the development and application in chemical kinetics of the tracer atom method, which has played a major role in the study of the mechanisms and rates of chemical reactions (A.I.Brodskii and S.Z.Roginskii). M.B.Neiman developed a kinetic version of the isotope method, which is particularly effective in the study of the sequence of stages in a complex chemical process and in the determination of the rate constants for elementary reactions and the concentrations of atoms and radicals.

Together with the publication of an enormous number of studies on chemical kinetics throughout the world, the unusual expansion of kinetic investigations in our country enabled N.N.Semenov to survey these chemically most important data in a monograph (Some Problems of Chemical Kinetics and Reactivity) (1958).

During the early period of the development of the theory of branched chain reactions, N.N.Semenov already pointed out the possibility of the occurrence of chain processes with energetically branched chains, which take place as a result of the reactions of vibrationally excited molecules—the products of the exothermic elementary stages of the chain process. Subsequently A.E.Shilov, A.M.Chaikin, V.I.Vedeneev, and G.A.Kapralova, showed that molecular fluorine reacts in the gas phase with a series of molecules, forming atoms and radicals. It was established that this may entail energy branching of two types: as a result of the unimolecular decomposition of the excited molecules into radicals (atoms) or the bimolecular interaction of the excited molecules with the initial molecules, also with formation of atoms and molecules.

The chemical laser was first constructed on the basis of the reaction of fluorine with hydrogen which takes place with energy chain branching (V.L.Tal'roze).

In the study of the kinetics of gas-phase reactions much attention has also been devoted to cracking processes. The development of ideas concerning the chain mechanism of the cracking of hydrocarbons and the study of the kinetic mechanisms of the elementary stages are associated with the investigations of V.V.Voevodskii and A.D.Stepukhovich of the kinetics and thermodynamics of the reactions of alkyl radicals.

The determination of the constants for elementary processes in the Earth's ozonosphere, responsible (in competition with the photochemical formation of ozone) for the maintenance of a steady-state ozone concentration, has become an important branch of V.L.Tal'roze's research. The elementary processes in the Earth's ozonosphere were modelled in the laboratory and their rate constants were measured.

In recent years the method of shock tubes has gained wide currency in the USSR and throughout the world. The elementary processes in the excitation of vibrations and the dissociation of diatomic (S.A.Losev) and polyatomic (A.A.Borisov and D.G.Knorre) molecules as well as electronic excitation and ionisation processes involving atoms and radicals (S.M.Kogarko) have been investigated by this method. The occurrence and characteristics of the "energetic" chain processes and the existence of critical conditions for the self-acceleration of the reaction as a result of the non-equilibrium distribution of the internal energies of the reactants was demonstrated directly in relation to the decomposition of NH_3 and N_2O (G.B.Manelis and A.P.Genich).

A.L.Tal'roze developed a method for the measurement of the rate constants for elementary reactions with the aid of a hydrogen maser. It is based on the determination of the rate of reaction from the change in the spin state of hydrogen on interaction of its atoms with non-paramagnetic molecules.

A theory of the kinetics of the initial stages of the chlorination of ethylene under non-stationary conditions has been developed and the possibility of obtaining vinyl chloride in the hydroxychlorination of ethylene in a single-pulse adiabatic compression apparatus has been demonstrated (A.Ya.Rozovskii and Yu.A.Kolbanovskii).

A "positronium" method for the investigation of the kinetics of fast chemical reactions in gas and condensed phases has been devised (V.I.Gol'danskii). The rate constants for the positronium atom formation reactions as well as the rate constants for the processes involving the excitation of the electronic levels of molecules have been determined.

A highly sensitive kinetic method for the determination of the rate constants for elementary reactions based on a combination of the intraresonator laser spectroscopy with flash photolysis has been devised and introduced into practice. The mechanisms and the rate constants for a series of elementary reactions with participation of the radicals $\dot{N}H_2$, $CH\dot{O}$, and $H\dot{O}_2$ and the excited radicals $\dot{N}H_2$, which play an important role in atmospheric processes, oxidation, and combustion, have been determined (O.M.Sarkisov).

The possibility of controlling gas-phase chain reactions by means of infrared laser radiation has been demonstrated experimentally. Selective bromination of methyl fluoride with respect to carbon isotopes under the influence of the continuous radiation of a CO_2 laser has been achieved (Yu.N.Molin).

Much interest has been shown in the study and description of the kinetics of non-equilibrium processes, which are important under the conditions of high temperatures and a high vacuum (for example, in the upper layers of the atmosphere). A theory of the non-equilibrium decomposition of diatomic molecules, taking into account the dependence of the probabilities of the vibrational transitions on the vibrational quantum number, has been proposed (E.E.Nikitin). The theory has been extended also to polyatomic molecules.

The vibrational temperatures and rate constants for the dissociation reactions of certain small molecules occurring under the conditions of a non-equilibrium distribution of energy have been calculated theoretically (N.M.Kuznetsov).

Apparatus with crossed molecular beams has been devised for the experimental study of elementary reactions under conditions where the chemical interaction of two species takes place in isolation and is not accompanied by effects involving the deactivation of molecules or secondary chemical reactions (V.N.Kondrat'ev and L.Yu.Rusin).

The differential cross-sections of the ion pair formation processes in the interaction of two heavy neutral species ($Xe + CsBr \rightarrow Cs^+Br^- + Xe$) have been measured in recent studies in the range of collision energies 4.5–7.5 eV. A significant influence of the mutual orientation of the species and of the masses of the colliding atoms on the process cross-section was observed. A dynamic model of the process occurring non-adiabatically on one potential energy surface was constructed on the basis of the experimental data. The calculation of this surface served as a basis for the trajectory modelling of the process in the subthreshold region where the dynamic limitations to the occurrence of the process are manifested most strikingly.

Liquid-phase reactions. The study of the liquid-phase oxidation of organic compounds occupies a notable place in the research into the kinetics of liquid-phase radical reactions.

The peroxide theory of slow oxidation processes put forward by A.N.Bakh at the end of the last century was subsequently frequently confirmed experimentally. In the 1940s K.I.Ivanov isolated peroxides from the oxidation products of many organic substances and studied their structure, properties, and reactions. G.A.Razuvaev's school has made a major contribution to the chemistry of the reactions of organoelemental and other peroxide compounds.

The systematic study of the kinetics and mechanism of the liquid-phase oxidation of hydrocarbons from the standpoint of the chain theory was begun in the 1950s (N.M.Emanuel', I.V.Berezin, D.G.Knorre, E.T.Denisov, Z.K.Maizus, E.A.Blyumberg, G.E.Zaikov, I.P.Skibida, A.B.Gagarina, and G.V.Karpukhina). A chain theory of the liquid-phase oxidation of organic substances was created and experimentally justified as a result of numerous investigations. Kinetic equations were obtained for chain oxidation reactions of compounds of different classes. General fundamental mechanisms of the autocatalytic, catalytic, and inhibited oxidation have been devised and numerous specific reactions have been studied experimentally. The rate constants for various elementary stages of the oxidation reactions of individual hydrocarbons and multicomponent systems have been determined and new types of elementary reactions (particularly in chain initiation and branching reactions) have been discovered. The influence of the solvent on the individual elementary reactions has been established and the role of specific and non-specific solvation of the reactant in homolytic reactions has been elucidated.

Hypotheses concerning the stimulation of slow chain oxidation reactions have been put forward and developed and a procedure has been suggested for the initiation of these reactions by adding O_3 and NO_2.

The liquid-phase reactions in open systems have been investigated, which is necessary for the creation of a scientific basis for continuous chemical technological processes.

A novel principle for the conversion of certain gas-phase reactions into reactions occurring under conditions of liquid-phase highly selective low-temperature oxidation at temperatures and pressures close to the critical parameters has been proposed.

The preparation of acetic acid and ethyl methyl ketone by the liquid-phase oxidation of butane aroused much interest in this connection. The synthesis of sulphuric acid by the liquid-phase oxidation of sulphur dioxide in the presence of catalytic amounts of nitric acid is based on the same principle. This method can be regarded not only as a procedure for the preparation of sulphuric acid but also as a method for the purification of industrial gases, since SO_2 is completely absent from the effluent gas.

Studies on the oxidation of binary and multicomponent mixtures of organic compounds, which are of practical importance, are being developed at a new, higher level with the aid of computers. The important role of alkyl radicals in processes involving the joint oxidation of hydrocarbons has been established.

The method of synthesis of epoxypropane by the oxidation of a mixture of propene and acetaldehyde is based on the joint oxidation principle. The hydroperoxy-radical formed in the oxidation of acetaldehyde serves as the epoxidising agent in the reaction with propene.

The mechanism of the action of many inhibitors has been established and the reactions of inhibitors (amines and phenols) in systems undergoing oxidation have been investigated. The important role of inhibiting radicals and of their interaction with the substance being oxidised in inhibited oxidation processes has been demonstrated. The reactions of inhibiting radicals have been studied by EPR and flash photolysis.

Critical phenomena are some of the most striking effects in inhibited oxidation. It has been observed that the inhibition period can change sharply after the attainment of the critical inhibitor concentration.

The phenomenon of synergism in the action of mixtures of inhibitors, i.e. a non-additive alteration of the inductive periods following a change in the ratio of the components of the inhibiting mixture, is exceptionally important for inhibited oxidation.

The phenomenon of the radical interaction of inhibitors, which underlies the mechanism of the synergistic effect, has been discovered. It consists in the regeneration of the more effective inhibitor as a consequence of the transfer of a hydrogen atom to its radical from the molecule of the less effective inhibitor.

Interest in the employment of complex metal compounds of inhibitors of liquid-phase oxidation and in the study of the mechanism of the metal complex inhibition has increased.

It has been established that the inhibition of oxidation reactions by metal compounds is due to two causes: the decomposition of the hydroperoxide into non-radical products, and, more frequently, the interaction of the free radicals with the inhibitors. The mechanisms of the metal complex inhibition have been established for a number of systems.

The nature of the chemiluminescence accompanying oxidation processes has been studied; it has been shown that it arises in the step involving the recombination of the peroxy-radicals. Chemiluminescence methods have been devised for the measurement of the kinetic parameters of the oxidation reactions (V.Ya.Shlyapintokh, R.F.Vasil'ev, O.N.Karpukhin, V.A.Belyakov, and I.F.Rusina).

Studies on liquid-phase oxidation have also been prosecuted vigorously at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences (INKhS) (A.N.Bashkirov and V.V.Kamzolkin) and the Institutes of the Academies of Sciences of Union Republics, namely the Ukraine (R.V.Kucher), Belorussian (N.I.Mitskevich), Azerbaijan (B.K.Zeinalov and T.N.Shakhtakhtinskii), and Estonia (M.Gubergrits), at branch institutes (V.K.Tsyskovskii, Kh.E.Khcheyan, D.N.Mushenko, E.D.Radchenko, and S.V.Sokolov), and at higher educational establishments, namely the Lensovet Leningrad

Institute of Chemical Engineering (V.A.Proskuryakov), the Mendeleev Moscow Institute of Chemical Engineering (N.N.Lebedev), the Yaroslavl Polytechnic Institute (M.I.Farberov), Gorky State University (Yu.A.Aleksandrov), and the Kazan Institute of Chemical Engineering (P.A.Kirpichnikov and N.M.Lebedeva).

R.V.Kucher and coworkers have been concerned with the analysis of the kinetics of the oxidation reactions of multicomponent mixtures. Data on the reactivities of a number of radicals and molecules have been obtained by the method of the joint oxidation of organic compounds of different classes (I.A.Opeida).

The kinetics of the joint oxidation of polycyclic aromatic hydrocarbons and phenols and of their forced degradation have been studied, which is very important for the solution of the problem of the protection of the environment; the studies of M.Gubergrits have been devoted to the creation of new methods for the purification of waste water and for the prediction of self-purification processes in the medium.

The role of coupled reactions in the oxidation of organic compounds is being systematically investigated (M.I.Mitskevich).

As before, much attention has been devoted to the investigation of the kinetics and mechanisms of the autoxidation of organoelemental compounds. It has been established that in many instances the oxidation of these compounds proceeds via a free radical chain mechanism. A relation has been discovered between the kinetics and the nature of the states of the organoelemental compounds in the reaction medium, the formation of complexes of organoelemental compounds with oxygen and other ligands, and the subsequent reactions of the oxygen complexes of the organoelemental compounds and of organoelemental peroxides via competing reactions. The oxidation reactions of ligands located in the coordination sphere of the heteroatom in the molecule of the organoelemental compound have been studied (Yu.A.Aleksandrov).

The manufacture of phenol and acetone, involving the stage in which isopropylbenzene is oxidised to the hydroperoxide, has been established in the USSR and the manufacture of synthetic aliphatic acids by the oxidation of paraffins is developing. The oxidation of cyclohexane to cyclohexanone is a component of the modern Soviet technology of the synthesis of caprolactam.

Methods have been proposed for increasing the efficiency of the extraction of petroleum from the ground on the basis of ideas concerning the mechanism of the liquid-phase oxidation of hydrocarbons. Liquid-phase oxidation within geological strata is being investigated as a method of displacing petroleum from such strata (E.A.Blyumberg and M.G.Bulygin).

The oxidation of organic compounds by ozone has been studied. The kinetics and mechanism of the reaction of ozone with the C–H bond and the nature of the intermediate labile species have been investigated. Ozone, an extremely efficient oxidant for many toxic compounds, is widely used nowadays for the purification of industrial waters and air before their release into water reservoirs and ejection into the atmosphere. The scientific basis of the decompositions reactions of tetraethyl-lead and other organoelemental compounds, phenols, and dyes has been discovered.

Methods have been proposed for the synthesis of highly pure dicarboxylic and monocarboxylic acids with the aid of ozone.

Effective catalysts have been found for controlling the reactions of ozone with organic compounds whereby undesirable processes can be suppressed and the mechanisms of the reactions of ozone can be altered radically.

New methods and instruments, promoting a wide-scale employment of ozone in analytical chemistry and scientific research, have been developed. The mechanism of the involvement of ozone in atmospheric processes and the influence of anthropogenic factors on the stability of the natural cycles involving ozone are being studied (S.D.Razumovskii, G.E.Zaikov, V.D.Komissarov, M.T.Drozdov, E.T.Denisov, Yu.A.Aleksandrov, B.V.Enel'yanov, V.A.Yakobi, I.K.Larin, and V.L.Tal'roze). The higher oxides of transuranic elements have been obtained with the aid of ozone (V.I.Spitsyn, A.D.Gel'man, and N.N.Krot).

Important research into the kinetics and mechanisms of heterolytic reactions in solution (nitration and sulphonation reactions, hydration of olefins, dehydration of alcohols, and isomerisation and cyclisation of unsaturated compounds) has been carried out in many scientific establishments and educational institutes. These include the Institute of Organoelemental Compounds of the USSR Academy of Sciences (INEOS) (A.N.Nesmeyanov, M.I.Kabachnik, and D.N.Kursanov), Institute of General Chemistry of the USSR Academy of Sciences (S.G.Mairanovskii), Institute of Chemical Physics of the USSR Academy of Sciences (M.M.Chirkov, M.I.Vinnik, and S.G.Entelis), the Karpov Physicochemical Institute (NIFKhI) (A.I.Shatenshtein and M.I.Temkin), Academy of Sciences of the Ukrainian SSR (A.I.Brodskii, E.A.Shilov, N.A.Izmailov, and M.M.Litvinenko), Moscow University (O.A.Reutov and I.P.Beletskaya), Leningrad University (T.N.Temnikova), and Tartu University (V.Palm).

An important branch of the kinetics of heterolytic reactions involves studies in the theory of acids and bases and acid catalysis. A.I.Shatenshtein put forward and justified the concept of the protolytic (acid–base) nature of the heterolytic hydrogen exchange reaction. It has been demonstrated that the simplest hydrogen substitution reactions have a mechanism in common with reactions such as metallation and base-catalysed exchange. A kinetic method has been proposed for the determination of the strength of very weak acids and bases such as hydrocarbons, which led to a re-examination of the traditional views on acids and bases. The nature of the catalytic activity of systems consisting of protic and aprotic acids was explained.

A.I.Brodskii's studies, devoted to isotope exchange reactions, led to the discovery of two different groups of reactions—the fast and slow isotope exchange reactions. Fast exchange is observed for compounds with an X–H bond (N–H, O–H, S–H, Cl–H) in which the atom X has a free electron pair.

N.I.Temkin and A.I.Gel'bshtein studied the kinetics and mechanisms of organic reactions under the influence of acids and salts. The temperature dependence of the acidity function has been determined for certain strong acids for the first time.

Studies were also made of the elementary reactions of ions in aqueous and non-aqueous media and the important role of ions as intermediate species in organic reactions catalysed by acids and bases was established (M.I.Vinnik).

Ya.K.Syrkin has made a major contribution to the development of the theoretical ideas about the mechanism of the elementary step in heterolytic processes. In order to explain the detailed mechanisms and kinetics of heterolytic reactions, he employed the concept of a cyclic transition state.

The large scale of research into the kinetics of heterolytic reactions in solutions is due to the importance of these processes for industry. E.A.Shilov studied the mechanism of the reactions of chlorine with organic compounds, which

constitutes the basis of the industrial synthesis of ethylene chlorohydrin. The decisive role of π-complexes in many reactions involving olefins has been established. It has been shown that reactions in which halogen halides add to compounds with a multiple bond are electrophilic or nucleophilic depending on the nature of the reactants and the solvent.

Ya.K.Syrkin and I.I.Moiseev discovered the direct oxidation of olefins to vinyl esters and the synthesis of acetals directly from olefins and alcohols. Olefins were oxidised to carbonyl compounds.

A series of studies by D.N.Kursanov, devoted to the mechanism of the dehydration of alcohols and the reactions of quaternary ammonium salts, showed that these processes proceed via a carbonium mechanism. Studies on hydride shifts made a major contribution to modern ideas about the hydride mobility of hydrogen in organic compounds.

Heterolytic reactions of nitro-compounds were investigated by V.M.Belikov.

N.M.Chirkov and V.I.Gol'danskii confirmed experimentally N.N.Semenov's idea of the possibility of homogeneous acid catalysis under heterogeneous conditions: a study was made of the kinetics (true kinetics uncomplicated by diffusion) of a series of important processes such as dimerisation, hydration, and hydrohalogenation of olefins in thin films of strong acids on an inert carrier.

An industrial synthesis of high-octane fuel on an acid film catalyst has been developed.

The influence of the medium in liquid-phase reactions, modelling the elementary step in heterolytic polymerisation and polycondensation processes, has been taken into account quantitatively.

It has been established in relation to the catalytic trimerisation of isocyanates P–N=C=O in solution in the presence of an amine–epoxide system that the cyclic product is formed on a complex-template produced beforehand and consisting of a cyclic trimer and primary active centres, which are produced as a result of the interaction between the components of the initial catalytic amine–oxide system (S.G.Entelis).

O.A.Reutov and I.P.Beletskaya examined the influence of the structures of the reactants and the role of solvation and ion pairs in electrophilic substitution reactions of organomercury compounds.

Ideas concerning bifunctional catalysis have been developed on the basis of an extensive study of the kinetics and mechanisms of acyl group transfer reactions (acylation of amines). It was shown that organic acids play the role of bifunctional catalysts in these processes (L.M.Litvinenko).

The investigation of the kinetics and mechanism of the classical heterolytic reaction, involving the acid and base hydrolysis of esters, from the standpoint of the relation between the structure of the esters, on the one hand, and the reactivity and role of the medium in these processes, on the other, has been continued (V.Palm). Correlation equations based on the principle of the linearity of free energy relations are widely used in describing such relations.

M.G.Gonikberg investigated the influence of pressure on the rate constants for liquid-phase reactions. It was established that the accelerating effect of the pressure rises with increase of the steric hindrance of the reaction. This is due to the partial mutual overlap of the van der Waals spheres of the atoms shielding the reaction centres in the activated complex. Pressure leads to an additional contraction on formation of the activated complex. These data served as the basis of a new method for the investigation of the structure and properties of the transition state and the mechanisms of organic reactions by kinetic studies at high pressures.

New novel fields of research, based on a detailed study of the mechanisms of chemical reactions, have arisen recently. The field of chemical physics, dealing with a wide variety of magnetic effects in chemical reactions, the role of magnetic interactions, and the behaviour of the magnetic moments of electrons and nuclei in chemical reactions, began to develop in the 1970s.

The energy of magnetic interactions in chemistry is negligible compared with the energy of thermal motion; this factor is the reason for the insufficient attention paid to the role of magnetic interactions in chemistry. However, these weak interactions control the behaviour of the spins of electrons and nuclei and therefore exert a strong influence on spin restrictions in chemical reactions.

The phenomenon of chemically induced dynamic nuclear polarisation in radical reactions occurring in a magnetic field, as a result of which the nuclear spins in the molecules of the products assume a preferred orientation, has been discovered. Either an anomalously strong absorption or coherent emission in the microwave frequency range are then observed in NMR (A.L.Buchachenko and E.T.Lipmaa). Emission has been observed in the photochemical reaction of porphyrin with quinone in a field of 25000 G (the emitter was the quinone molecule and the emission wavelength was 3 m) and in the thermal decomposition of benzoyl peroxide in a 15000 G field (the emitter was the benzene molecule and the wavelength was 5 m) (A.L.Buchachenko).

The influence of external magnetic fields on the rate and direction of reactions proceeding via the formation of a pair of magnetic species—radicals or radical-ions—has been demonstrated. The magnetic field influences the spin state of the pair of species.

The method of magnetic resonance detected from the change in the reaction rate (RCDMR) has been proposed for the investigation of the reactions of short-lived radical species. Its essential feature is that, by carrying out the reaction in the resonator of a special EPR spectrometer, it is possible to alter the spin state of the intermediate species and hence the yield of products (E.L.Frankevich).

The dependence of the rate of radical reactions on the magnetic moment of the nuclei and the energy of the electron–nuclear magnetic interaction has been observed (Yu.N.Molin and A.L.Buchachenko). In contrast to the classical isotope effect, the new isotope (magnetic or nuclear spin) effect is related to the difference between the magnetic properties of the isotope nuclei and not the difference between their masses. A new principle of enrichment in magnetic isotopes has been proposed on its basis and new methods for the investigation of the mechanisms of chemical and biochemical processes have been devised.

The ^{17}O magnetic isotope effect arises, for example, in the liquid-phase oxidation reaction of organic compounds at the peroxy-radical recombination stage: the $R^{17}O^{16}O$ radicals recombine faster than the $R^{16}O_2$ or $R^{18}O^{16}O$ radicals:

$$R^{17}O^{16}O + R^{16}O_2 \rightarrow {}^{17}O{-}{}^{16}O + \text{products};$$
$$R^{16}O_2 + R^{16}O_2 \rightarrow {}^{16}O{-}{}^{16}O + \text{products}.$$

As a result, molecular oxygen is enriched in the ^{17}O isotope in the course of its consumption in the oxidation reaction. During the oxidation of ethylbenzene, the enrichment in ^{17}O was 13%, which exceeds by two orders of magnitude the quantity due to the classical mass isotope effect.

The kinetics and mechanism of spin exchange in the condensed phase, simulating the individual stages of a homogeneous-catalytic process, have been investigated

comprehensively. A new class of chemical reactions—tunnel electron transfer reactions over large distances (15–30 Å)—has been discovered and investigated (K.I.Zamarev and R.F.Khairutdinov).

Studies on the methods of chemical microwave spectroscopy in weak magnetic fields have been continued. A unique NMR spectrometer has been constructed for the investigation of chemical processes in the Earth's magnetic field (Yu.N.Molin).

The combined development (in terms of apparatus, theory, and experiment) of a new microwave spectroscopic method—the method of the spin echo arising under the influence of ultrahigh frequency radiation—was achieved for the first time at the Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences. The method leads to unique possibilities for the detection and analysis of weak and exchange interactions in radical pairs (Yu.D.Tsvetkov and A.G.Semenov).

Studies in a new field—the NMR spectroscopy of paramagnetic species—are being developed (Yu.N.Molin). The method is highly sensitive and makes it possible to determine not only the magnitude but also the sign of the spin density.

Solid-phase reactions. Studies on the kinetics of reactions in the solid phase (solid state chemistry), associated with the development of theoretical chemistry and solid state physics and also with the application of new physical methods in chemical kinetics, have been widely developed.

V.I.Gol'danskii developed a radiochemical method for the study of the kinetics of fast reactions in the solid phase—emission Mössbauer spectroscopy. The method makes it possible to measure the rates of chemical reactions over a period from 10^{-6} to 10^{-9} s. The study of the rates of oxidation-reduction reactions involving iron cyanide complexes over a wide temperature range (4–400 K) made it possible to obtain quantitative kinetic characteristics of the interionic electron transfer in ferro-ferricyanides and to detect a low-temperature quantum limit to the rates of these reactions.

An anomalously fast polymerisation in the solid phase and in certain liquid systems, where the monomer molecules are fairly well ordered, has been discovered and investigated: explosive low-temperature polymerisation reactions in the phase transformations of solid monomers and the polymerisation of solid monomers at high pressures in combination with shear deformation (N.S.Enikolopov, V.I.Gol'danskii, V.A.Kabanov, and A.B.Abkin).

The rate of polymerisation chain propagation has been studied in solid formaldehyde over a wide temperature range, down to the boiling point of liquid helium (4.4 K). The time taken to add each chain unit in the temperature range 80–150 K increased with decrease of temperature in accordance with the Arrhenius law, the activation energy amounting to 2000–2500 cal mol^{-1}, and reached 10^{-5} s at 80 K. On further decrease of temperature, a deviation from the Arrhenius law was observed. Below 10 K, the time required for an increment by one unit constituted one hundredth of a second, which exceeded by many orders of magnitude the calculated value. Thus it was found that, instead of the complete freezing of the reactivity, at the lowest temperatures the rate of an exothermic chemical reaction tends to a measureable limit.

The phenomenon of the low-temperature limit to the rates of chemical reactions is of quantum (tunnel) origin. Combined studies are being performed on the role of quantum (tunnel) effects in the elementary stages of low-temperature reactions with the transfer of electrons, atoms, and molecular groups via the tunnel mechanism. New versions of the mathematics of polychromic [? Ed.of Translation] kinetics have been developed for the quantitative description of tunnel and thermally activated solid-phase reactions.

Studies on low-temperature chemistry have acquired increasing importance. A wide range of chemical reactions (halogenation and hydrohalogenation of olefins), which occur at high rates at temperatures of the order of 77 K, have been investigated. Studies have been made of the kinetics and mechanism of the hydrohalogenation of olefins in non-polar media at low temperatures. The phenomenon of the inversion of the selectivity of the non-initiated hydrobromination, consisting in the fact that, depending on the reaction ratio, the reaction can be carried out quantitatively either in accordance or contrary to the Markovnikov rule, has been observed for the hydrogen bromide addition reactions.

The possibility of the catalytic hydrochlorination of olefins at high rates and with 100% yield of products at temperatures up to 140 K has been established. It has been shown that the low-temperature solid-phase reactions of atomic magnesium with organic chloro-derivatives are greatly accelerated at the phase transition points. The formation of paramagnetic species, including alkyl radicals, in these reactions has been demonstrated for the first time by EPR (G.B.Sergeev).

The unusual phenomenon of mechanochemical explosion has been observed for the chlorination of hydrocarbons, the hydrobromination of olefins, and polymerisation in vitreous and polycrystalline systems. It has been established that local brittle breakdown of solid irradiated specimens at 4.2–77 K leads to an explosive increase in the rate of the chemical reaction, which rapidly embraces the entire specimen (I.M.Barkalov).

The role of different kinds of crystal lattice defects in processes occurring in solids and on their surfaces has been studied (G.B.Manelis, A.V.Raevskii, and S.Z.Roginskii).

Studies in the field of solid-state chemistry have been carried out by V.V.Boldyrev. The dependence of the physicochemical properties of solids and of their reactivity on the characteristics of the real structure have been investigated: transfer processes in the solid phase associated with chemical reactions as well as phase transformations accompanied by chemical reactions in the solid substance.

The causes of the localisation and autolocalisation of processes have been studied, which leads to the possibility of specific regulation of topochemical reactions not only in time but also in space.

The research into the kinetics and mechanism of reactions initiated in different solid organic and inorganic materials by applying mechanical stresses has been expanded (P.Yu.Butyagin).

The theoretical aspects of the tribochemical breakdown of solids have been examined. The dependence of the increase of the chemical reactivity of a solid as a result of a mechanical influence on the accumulation of defects in its crystal structure has been demonstrated.

A series of new models of elementary and macrochemical processes, whereby experimentally observed phenomena can be explained and new effects predicted, have been developed for chemical solid-phase reactions.

Many investigators have used EPR to study the kinetics of the reactions of radicals in solid media. New phenomena, such as an increase of the reactivity of the radicals at the phase transition temperatures of the solid matrices and the relay transfer from a free valence, have been discovered.

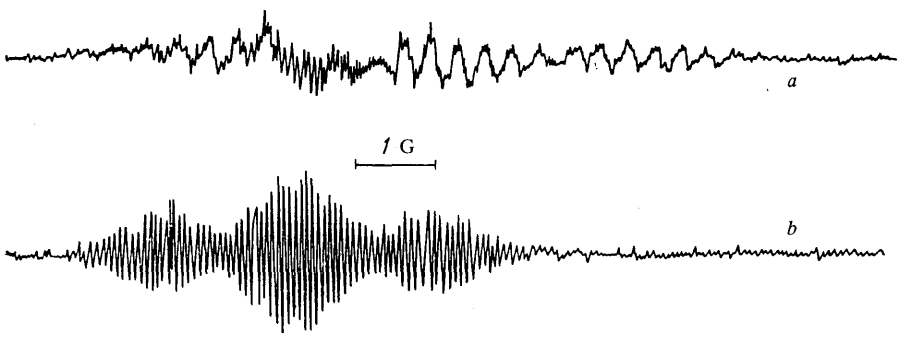


Figure 10. EPR spectrum of the stable 2,5-di-t-butyl-*p*-benzosemiquinone radical (the second derivative of the absorption signal) obtained with the aid of the usual EPR spectroscopy (*a*) and the EPR spectroscopy based on the parametric detection of the transitions between non-stationary spin states of the paramagnetic centres (*b*).

Highly-sensitive versions of the EPR technique have been devised whereby one can obtain new information about reactions and paramagnetic species in the condensed phase. Thus a version of EPR spectroscopy, based on the paramagnetic detection of transitions between non-stationary spin states of paramagnetic centres, has been devised. Signals of individual radicals can be isolated from a complex EPR spectrum by this method (Fig.10) (L.A.Blyumenfel'd).

The "two spin probe" or "oriented spin probe" methods have been proposed for the investigation of ultraslow molecular movements in the solid phase (Ya.S.Lebedev).

5. Thermal Explosion, Combustion, and Detonation

One of the most important fields in chemical physics is the science of combustion and explosion, which has undergone a comprehensive theoretical and experimental development in the research by Soviet scientists.

The theory of thermal explosion in an exothermic reaction was formulated by N.N.Semenov almost simultaneously with the theory of chain inflammation. The theory is based on the concept of the breakdown of thermal equilibrium in the system, an excess of the incoming heat relative to the outgoing heat, which leads to a progressive increase of the rate of reaction up to explosion. Mainly the quantitative aspect of the theory of thermal explosion was developed further in the studies of Ya.B.Zel'dovich, D.A.Frank-Kamenetskii, and O.M.Todes; specific characteristics of the process, induced by the complex mechanism of the chemical reactions and the characteristics of the heat exchange, were analysed. Subsequently A.G.Merzhanov developed a theory of thermal explosion in relation to processes in the condensed phase and investigated the quasi-stationary and non-stationary regimes of various types as well as heat exchange conditions.

Ya.B.Zel'dovich devised a thermal theory of the propagation of flames in gases, according to which the chemical reactions which determine the rate of the overall process take place in a narrow zone near the maximum temperature. The principal characteristics of the combustion have been obtained and a dependence of the rate of combustion on pressure and the initial temperature was found. The stability of the process and the uniqueness of the solutions were studied in detail and the necessary mathematics were devised.

In the study of the combustion of volatile explosives (A.S.Belyaev), it was shown that the explosive initially evaporates as a result of the heat arising from the zone of the flame and the principal reactions occur in the gas phase; consequently the main characteristics of the combustion of volatile explosives are analogous to the combustion of gases.

The combustion of powders has been studied in detail. It has been established (B.P.Zhukov and P.F.Pokhil) that in this instance the stages determining the rate and the fundamental characteristics of the combustion are chemical reactions occurring in a viscous liquid layer of the condensed phase on the surface of the burning powder. It was observed that the combustion process takes place in stages.

The complex mechanism of the combustion of condensed systems has been investigated and a quantitative theory of the combustion of such systems has been developed on this basis (G.B.Manelis and A.G.Merzhanov). The regulating role of dispersion and evaporation (sublimation) processes and the nature of the multistage mechanism of chemical combustion reactions when the role of the reactions in the condensed phase is decisive has been elucidated.

A thermal theory of ignition has been devised and non-stationary phenomena during combustion (various kinds of instabilities, inflammation, quenching, etc.) have been investigated.

Since the studies by V.N.Kondrat'ev (reactions in flames) and S.Z.Roginskii (decomposition of explosives), there has been vigorous research into the kinetics and mechanisms of chemical reactions occurring during combustion. The thermodynamics of combustion products have been studied in detail (L.V.Gurvich) and studies have been made of the quantitative characteristics of the chemical reactions of different classes of substances at high temperatures (R.I.Soloukhin, G.B.Manelis, and A.A.Borisov) and the thermal decomposition of explosives. The detailed reaction mechanism has been established and the relation between the rate of reaction and the structure of the explosive has been determined (S.I.Dubovitskii and G.B.Manelis).

The research into elementary chemical reactions, energy transfer processes, and non-equilibrium chemical reactions in combustion and explosive processes in ultrasonic fluxes of reacting gases has developed vigorously. Computational methods and modern methods for the diagnostics of rapid non-equilibrium processes have been devised.

The combustion mechanism has been investigated and a theory of the inflammation and combustion of liquid drops and particles of metals as well as their combinations has been set up (G.A.Varshavskii, O.I.Leipunskii, A.G.Merzhanov, L.M.Stesik, and B.I.Khaikin).

The combustion of light fuel in engines has been studied. The high chemical reactivity of the incomplete combustion products of the fuel mixture has been demonstrated. A new method of organising combustion processes—fore-chamber flame ignition—has been proposed on this basis (A.S.Sokolik and A.N.Voinov). This principle has found application in both internal combustion engines and in furnaces and other apparatus of different kinds (L.A.Gussak).

The results of studies in the field of combustion have been very important for the development of safety techniques. Methods for the regulation of the combustion process have been devised in relation to problems of safety as regards fire and explosion. Conditions have been found whereby safety against explosion can be ensured in the transport of acetylene in pipelines and in the smelting of titanium in electric arc furnaces. Engineering methods for calculations on various technological processes in chemical and related branches of industry, which rule out thermal self-inflammation, have been devised on the basis of the modern theory of thermal explosion.

The problem of the propagation and quenching of fires has been studied. A physicomathematical model of the dynamics of the propagation of large-scale forest and city fires has been set up. The mechanism of the quenching of a gaseous flame under the conditions of complex heat exchange has been studied. A new type of firebreak has been developed for the solution of technical fire protection problems.

Theoretical investigations have been carried out and the dynamics of large-scale eddy movements in the atmosphere, due to the effluent combustion products in major fires and volcanic erruptions, have been studied (Yu.A.Gostintsev). A physicomathematical model of global eddy movements in the atmospheres of the giant planets (Jupiter and Saturn) has been set up on this basis.

One of the most important fields of research into explosive processes involves the study of detonation. A general theory of detonation has been developed in the studies of Ya.B.Zel'dovich and A.S.Kompaneits. Yu.B.Khariton formulated the principle of the equality of the duration of a chemical reaction and the time taken by the products, determining the limits of the propagation of a stable detonation, to move apart has been formulated and has become widely familiar. The phenomenon of the instability of a planar detonation front in gases (A.I.Shchelkin and Ya.K.Troshin) and in liquid explosives (A.N.Dremin) has been discovered and investigated. The structure and mechanism of the formation and propagation of shock waves in various media, their mechanical effects, and the dependence of the maximum pressure in the wave on the weight, charge, and location of the explosion have been studied (M.A.Sadovskii).

The mechanism of the explosion of the explosive as a result of mechanical influences has been discovered. The phenomenon is based on the formation of "hot points" in the plastic deformation of the explosive on impact and compression of the bubbles of gaseous inclusions, etc. with subsequent thermal inflammation in individual centres and the propagation of the process in the main bulk of the substance (K.K.Andreev and V.K.Bobolev).

The characteristics and conditions of the transition from combustion to detonation have been investigated and methods have been found whereby systems can be acted upon to hinder the transition to explosive regimes.

The processes and methods of the chemistry of combustion and explosion have begun to find extensive applications in new fields during recent years.

The fundamental features of the formation of artificial diamonds have been discovered (O.I.Leipunskii).

Methods and devices have been developed for flame drilling and thermal methods of acting upon petroleum-bearing seams, in particular the method of combustion within the seam in order to intensify the extraction of petroleum, have been developed (A.V.Talantov).

A fundamentally new, progressive technological method for the preparation of compounds in the combustion wave—the method of self-propagating high-temperature synthesis—has been created. Compounds of metals with nitrogen, hydrogen, boron, silicon, and carbon have been obtained by this method. The materials produced are highly fire-resistant, chemically stable, and very hard at high temperatures (A.G.Merzhanov); they are used in the manufacture of abrasives, solid alloys, and wear-resistant coatings.

Shock wave industrial methods for the synthesis of "black boron", a modification of boron nitride used in industry for the preparation of unique cutting instruments, as well as a shock wave method for the synthesis of diamonds have been developed on the basis of extensive studies of the processes occurring in shock waves (A.N.Dremin).

6. Catalysis

Homogeneous catalysis. The research into the mechanism of homogeneous catalysis was initiated in our country by the work of E.I.Shpital'skii, who was one of the first to suggest and justify the importance of the formation in the catalytic system of intermediate complexes with controllable properties and having different compositions, structures, and activities. Shpital'skii's ideas were supported in subsequent years by numerous pieces of experimental evidence in relation to a large number of homogeneous catalytic processes.

Physicochemical methods, namely ultraviolet spectroscopy, EPR, NMR, etc. are nowadays widely used in study of the compositions and the geometrical and the electronic structures of the unstable intermediate complexes.

The role of cyclic four- and six-membered intermediate donor–acceptor complexes of the initial substances with the catalyst has been demonstrated by E.A.Shilov and Ya.K.Syrkin.

A detailed study of the kinetics and mechanism of the selected oxidation of olefins by palladium salts made it possible to characterise quantitatively the elementary stages of this catalytic process and to elucidate the role of the intermediate σ- and π-complexes and has led to the creation of the theoretical foundations of metal complex catalysis.

A group of reactions involving the selective oxidation of olefins by palladium salts to valuable oxygen-containing compounds has been discovered. The manufacture of vinyl acetate from ethylene and acetic acid by this method has been widely applied in many countries (Ya.K.Syrkin and I.I.Moiseev).

The general principles of the action of active homogeneous metal complex catalysts have been formulated as a result of numerous investigations: their ability to form complexes with reactants, the weakening of the bonds to be dissociated, symmetry resolution, and the possibility of many-electron processes. The latter property obtains in polynuclear complexes and is necessary for many catalytic oxidation-reduction reactions. The ligands in the inner and outer spheres of the metal complex regulate its activity and selectivity by altering the stereochemistry of the catalytic

step, the charge on the central metal atom, and the conditions of electron transfer. These general principles of metal complex catalysis have been examined in greater detail in relation to catalytic oxidation, polymerisation, oligomerisation, and hydrogenation reactions.

The theory of the action of homogeneous catalysts in liquid-phase oxidation reactions has been widely elaborated. The concepts of the involvement of the catalysts in all the stages of the chain oxidation process have been justified.

The formation of intermediate complexes of the catalysts with oxygen, peroxy-radicals, and hydroperoxides in liquid-phase oxidation reactions of hydrocarbons has been proved theoretically and experimentally and their role in the overall catalytic oxidation process has been demonstrated.

The phenomenon of the dual function of the catalyst in the process, namely the transition from the region of positive catalysis at low catalyst concentrations to the region of "negative catalysis" (inhibition) with increase of the metal compound concentration, has been discovered and investigated. This initiated the development of a new field of metal complex inhibition. The hypothesis that the maximum selectivity of the oxidation reaction can be achieved when the latter occurs within the coordination sphere of the metal without the liberation of free radicals into space is being developed. The catalytic oxidation of certain organic compounds in alkaline media can apparently proceed via this mechanism.

Catalysis by mixtures of variable- and constant-valence metal compounds in the liquid-phase oxidation reactions of aromatic alkyl-substituted and naphthene hydrocarbons is being investigated by N.I.Mitskevich and V.A.Proskuryakov. It has been established that constant-valence metal compounds are capable of activating the catalytic system in many instances as a result of the formation of complexes with variable-valence metal compounds.

Low-temperature coupled oxidation systems with participation of metal complexes, whereby a considerable selectivity can be achieved in the oxidation of cyclohexane and n-alkanes to alcohols with low conversions, have been proposed (A.E.Shilov).

The employment of the principle of coupling in a single catalytic system of an exergonic oxidation reaction with an endergonic non-oxidative process makes it possible to carry out thermodynamically favourable reactions (I.I.Moiseev). For example, the dehydration of a carboxylic acid to an anhydride at low temperatures can be carried out by coupling it with the oxidation of carbon monoxide, ethylene, etc.

In the study of the catalytic oxidation of ascorbic acid in the presence of copper salts (A.P.Purmal') and also of the geometrical and positional isomerisation of olefins catalysed by palladium salts, a new type of chain processes was observed, in which the compounds of metals in an unusual oxidation state and not free radicals play the role of chain carriers.

In a study of acid catalysis, in particular catalysis by Lewis acids, N.M.Chirkov concluded that intermediate π-complexes of the olefins with H^+ are formed.

The principal characteristics of nucleophilic catalysis in aprotic media have been established. It has been shown in relation to the acyl transfer reaction that the formation of ion pairs having a high reactivity, which is to a large extent determined by the nature of the anion within the ion pair, plays an important role in the process in non-aqueous media (L.M.Litvinenko).

The discovery of the catalytic nitrogen fixation reaction under mild conditions is important (M.E.Vol'pin and A.E.Shilov): for example, when nitrogen interacts with organotitanium compounds, amines are formed. Aniline, toluidines, and other aromatic amines can be obtained in this way.

Homogeneous systems based on vanadium(II)–polyphenol systems, which reduce molecular nitrogen to ammonia in aqueous media, have been discovered (A.E.Shilov). Experimental apparatus for the synthesis of hydrazine by the reaction of nitrogen with vanadium hydroxide has been constructed.

New catalysts for the selective chlorination of alkanes by molecular chlorine and CCl_4 in the liquid phase have been proposed by M.L.Khidekel'. It has been found that many halogen-containing iron compounds, incorporating metal ions in different oxidation states, for example hexakis(acetonitrile). .iron(II) bis(tetrachloroferrate) $[Fe(II)(CH_3CN)_6]$. .$[Fe(III)Cl_4]_2$, as well as other complexes of iron containing dimethylformamide or dimethyl sulphoxide as the neutral ligand, exhibit a high catalytic activity in chlorination reactions and make it possible to obtain different chloroalkanes with a high selectivity. A characteristic feature of the action of these catalysts consists in the fact that the interaction of the reactants proceeds via an intermediate stage in which free radicals, stabilised in the coordination sphere of the catalyst, are formed.

A novel method for the synthesis of various aromatic amines by the liquid-phase hydrogenation of nitro-compounds has been developed. This method has been used to manufacture the starting materials for the synthesis of highly efficient herbicides (M.L.Khidekel' and A.A.Brikenshtein).

Studies involving the synthesis of metal complex catalysts similar in their efficiency and selectivity to enzyme systems are being prosecuted. The possibility of the reaction of conjugated dienes with SO_2 and NH_3 to form linear and cyclic sulphones and primary, secondary, and tertiary amines in the presence of phosphine complexes of palladium has been demonstrated.

B.A.Dolgoplosk completed a series of investigations into the synthesis and properties of organometallic compounds of transition metals (Ni^{2+}, Cu^{3+}, Cu^{2+}, Ti^{4+}, Ti^{3+}, Mo^{4+}, W^{4+}, V^{3+}, etc.), used as catalysts for the stereospecific polymerisation of dienes. The mechanism of stereoregulation and the nature of the active centres with different selectivities of action have been elucidated.

It has been established that the reactions of olefins with ring opening and metathesis of olefins constitute a new type of chain processes with a long chain comprising 10^5–10^6 units and initiated by carbene complexes of transition metals. Features characteristic of other chain reactions are typical for this process; in particular, it can be inhibited when more stable carbene complexes are used. Small amounts of compounds of the type $CH_2 = CHY$, where Y = OR, $Si(CH_3)_3$, etc., can also be used as process inhibitors.

New methods have been proposed for the catalytic synthesis of macrocyclic compounds, strained highly condensed polycyclic hydrocarbons, and linear polyene alcohols, amines and organosilicon compounds using homogeneous catalysts based on transition metal complexes.

In recent years much attention has been devoted to the study of the role of polynuclear (cluster) compounds in catalysis and the use of clusters as catalysts (A.P.Purmal', A.E.Shilov, O.N.Temkin, and I.I.Moiseev). It has been shown that a phosphene complex of palladium containing five palladium atoms and having a composition of the type $(PhP)_2Pd_5$ as well as a phenanthroline complex of palladium containing ten palladium atoms and having a composition of the type $[Pd_{10}(Phen)_4(O_2)_3](OAc)_3$ exhibit a high catalytic activity in the hydrogenation of olefins. A novel mechanism of catalysis by clusters has been discovered: in contrast to heterogeneous catalytic hydrogenation reactions, in the first

stage of the reaction catalysed by clusters a complex of the cluster with the substrate, which subsequently reacts with hydrogen, is formed in all the cases investigated and not the palladium hydride complex (I.I.Moiseev and A.S.Berenblyum).

A new field in the study of metal complex catalysis involves the creation of heterogenised (immobilised) metal complex catalysts. Such catalysts combine the advantages of the traditional homogeneous and heterogeneous catalysts. Both inorganic compounds and polymers can be used as carriers for the metal complexes. In the case of polymers, the employment of the specific features of the macromolecules for the fixation of the metal complexes ensures a high degree of structural correspondence and compatibility of the structures of the matrix and the substrate, which increases the efficiency of the catalysis. The fixation of complexes on the surfaces of carriers makes it possible to regulate the properties of the catalyst by altering the degree of its distribution on the carrier, by stabilising unusual valance forms of the metals, and by altering the steric configuration of the metals.

Various methods for the immobilisation of metal complexes have been developed (G.V.Lisichkin and A.D.Pomogailo).

The immobilised metal complexes $VO(C_2H_5O)_3$ or $Ti(OC_4H_9)_4$–$Al(C_2H_5)_2Cl$ on various polymeric carriers increase the activity and stability of the catalyst in the polymerisation reactions of ethylene, dienes, and acetylenic monomers (F.S.D'yachkovskii).

The fixation of complexes on metal oxide carriers can lead in certain cases to the inversion of their stereospecificity in polymerisation processes (B.A.Dolgoplosk).

New gel catalysts, which consist of metal complexes immobilised in a mosaic polymeric gel and catalyse the chemical reactions of unsaturated hydrocarbons, have been synthesised (V.A.Kabanov). The activity of such systems greatly exceeds that of catalysts of the Ziegler–Natta type. The catalysts are distinguished by a high thermal stability.

The structures and physicochemical properties of paramagnetic metal complexes with various complex-forming polymers [polyvinylpyridines, polyethyleneimine, and poly(acrylic acid)] have been investigated. Such complexes, immobilised on network polymers, are used as semiheterogeneous catalysts and also for the selective sorption of certain metal complexes and ions (V.A.Kabanov and K.I.Zamaraev).

Novel polymeric catalysts based on polyphenylenes and low-valence Group VIII metal compounds have been created. These catalysts exhibit a high selectivity in the hydrogenation and hydroxylation reactions of olefins and dienes.

Unusual heterogenised metal complex catalysts have been obtained on the basis of complexes of graphite with transition metals. It has been found that such involved graphite compounds have a high activity in the dehydrogenation of alcohols, the hydrogenation of olefins, acetylenes, and carbon monoxide, and in the synthesis of ammonia and other reactions. They effectively catalyse the conversion of graphites into diamond (M.E.Vol'pin).

Enzyme catalysis. Much attention has been devoted to the study of the structure of enzymes and the kinetics and mechanism of the action of enzyme systems. The studies by L.A.Nikolaev of the catalase, peroxidase, and oxidase properties of catalysts with comparatively simple structures have played an important role in this field. The concept of two- and many-electron processes in the coordination spheres of metals, put forward by A.E.Shilov and A.P.Purmal', proved to be extremely useful for the explanation of the significant decrease of the activation energy of the reaction in the case of enzyme processes involving a mechanism with molecular catalysis. The application of various physicochemical methods made it possible to construct a model of the system of active centres of the enzyme nitrogenase, which acts as a kind of "switching device" switching from the one-electron to the four-electron mechanism of nitrogen fixation (G.I.Likhtenshtein).

The chemical mechanisms of the biological fixation of nitrogen by nitrogenase and of hydroxylation with participation of cytochrome P-450 have been examined. New hydroxide systems which effectively reduce nitrogen to ammonia, hydrazine, and organonitrogen compounds have been discovered. The reduction of carbon dioxide to formaldehyde by aluminium amalgam in the presence of titanium(III) ions has been studied. Hypotheses have been put forward concerning the principles of the construction of catalysts for these reactions.

Studies have been made in which the decisive role of conformationally non-equilibrium states of protein macromolecules in enzymic catalytic reactions has been established (L.A.Blyumenfel'd).

Studies on the principles of the action of the nucleophilic active centre of the enzyme chymotrypsin made it possible to justify a new mechanism of the acceleration (by several orders of magnitude) of the acylation of surfactants by micelles as a result of solubilisation concentration—the so-called micellar catalysis. A kinetic theory of micellar catalysis has been proposed (I.V.Berezin and K.Martinek).

Yet another field in the simulation of enzymic catalytic processes involves the application of metal complex catalysts to the regulation of biochemical processes (M.E.Vol'pin). Synthetic catalysts capable of functioning in the living cell and causing a specific alteration of its metabolism have been created. Catalysts for the oxidation of the principal components of the respiratory chain (nicotine-adenine dinucleotide NADH, coenzyme Q, and cytochrome c), capable of propagating the process under physiological conditions (aqueous solutions at neutral pH) have been found (on the basis of cobalt compounds). The catalyst selectively "removes" electrons at the level of coenzyme Q and transmits them to oxygen by-passing the enzyme chain. The rate of the catalytic process is comparable to the rate of the enzymic reaction.

The catalytic action of metal complexes on the photosynthetic process has also been observed. In this case the source of electrons is a molecule of bacteriophyll excited by light. With the aid of certain complex catalysts, it has been possible to accelerate the light-initiated transport of electrons and to increase the yield of energy in photosynthesis.

Ideas concerning the role of four-electron processes in the formation of oxygen in plant synthesis are being developed by A.E.Shilov. A very simple model of the reaction of manganese in photosynthetic systems, involving the formation of dinuclear complexes incorporating manganese(IV) and manganese(VII), has been developed.

B.P.Belousov and A.M.Zhabotinskii discovered vibrational chemical processes based on the oxidation of malonic or other dibasic acids by cerium or manganese ions in the presence of BrO_3^- ions; these processes can be used as models of autooscillatory regimes in biological systems. K.B.Yatsimirskii observed the catalytic action of microamounts of ruthenium compounds in such systems. The use of the catalyst makes it possible to alter the oscillation frequency and the duration of the induction period, which can be regarded as a model of the regulation of oscillatory rhythms.

The acceleration of electronic processes by biological catalysts (bioelectrocatalysis) has been observed. It has been shown that enzymes catalyse electrochemical reactions via a mechanism involving direct electron transport from the

electrode to the active centres of the enzymes. Processes involving the electrochemical ionisation of hydrogen with participation of hydrogenase, the ionisation of oxygen with participation of oxidase, and the ionisation of hydrogen peroxide with participation of peroxidase have been achieved on this basis in the presence of chemically inert carbon surfaces. A theory of bioelectrocatalysis has been developed on the basis of the concept of electron tunnelling over long distances to non-conducting layers (lipid monolayers up to 25 Å thick) (I.V.Berezin and S.D.Varfolomeev).

The mechanism of the functioning of enzymes on a surface has been examined. The theoretical and experimental principles of the adsorption immobilisation of enzymes are being elaborated (O.M.Poltorak).

A new field in catalysis, namely catalysis by immobilised enzymes, has been widely developed in studies by I.V.Berezin. The principle of the stabilisation of enzymes by incorporating them in polymer gels has been proposed; the effective rate constant for the thermal inactivation of enzymes then diminishes by many orders of magnitude. This makes it possible to employ enzymes in reactors and to carry out chemical reactions under continuous conditions. A large number of carriers for the immobilisation of enzymes—natural compounds, synthetic organic polymers, and inorganic sorbents—have been proposed and investigated.

The application of immobilised biocatalysts makes it possible to solve many important problems in the field of fine organic synthesis, for example, in the creation of new antibiotics, the synthesis of essential and modified aminoacids, etc. Systems have been developed for the mechanical and light-induced initiation of enzymic processes on carriers, including processes with autoactivation of enzymes, which makes it possible to amplify weak primary signals by a large factor. A light-sensitive material suitable for photographic purposes has been produced on the basis of immobilised enzymes (N.F.Kazanskaya).

The modification of enzymes by biologically compatible polymers lowers their antigenic properties together with the increase of their thermal stability, which leads to applications of enzymes as medicinal preparations. A series of such preparations have been produced, among which the most effective proved to be "streptodekaza" [streptodecase?]—immobilised streptokinase (a thrombus decomposing enzyme) (E.I.Chazov, I.V.Berezin, V.M.Smirnov, K.Martinek, and V.P.Topchilin). Immunoenzymic analysis makes it possible to detect ultralow concentrations of physiologically active compounds (down to 10^{-16} M) and is used in other analytical investigations (A.M.Egorov and N.N.Ugarova).

Heterogeneous catalysis. Heterogeneous catalytic reactions constitute the basis of the majority of modern industrial chemical and petrochemical processes and in the first place large-scale processes such as cracking and reforming, the formation of the products and intermediates of major organic synthesis by oxidation, dehydrogenation, dehydration, isomerisation, alkylation, dealkylation, etc.

The vigorous study of catalytic processes, began in our country after 1917, was based on the activities of distinguished research chemists—V.N.Ipat'ev, L.V.Pisarzhevskii, N.D.Zelinskii, S.V.Lebedev, and B.A.Kazanskii.

The most important stage which initiated the study of the catalytic chemistry of hydrocarbons arose as a result of the research by N.D.Zelinskii and his school. As a result of the discovery of dehydrogenation catalysis and the irreversible catalysis of a series of hydrogenation, isomerisation, dimerisation, polymerisation, hydrogenolytic, and other reactions, catalytic synthesis has occupied a leading place in organic chemistry since the 1930's (N.D.Zelinskii, B.A.Kazanskii, and A.F.Plate).

In subsequent studies attempts were made to seek a general approach to the investigation of the mechanisms of catalytic reactions and a number of theories of heterogeneous catalysis were devised.

A.A.Balandin's multiplet theory, based on the principles of geometrical and energetic correspondence in the interaction of the reactants with the catalyst, determined the trend in many studies in the field of catalytic synthesis.

L.V.Pisarzhevskii created the electronic theory of catalysis. The idea of the involvement of the electrons of the catalyst in catalysis and of the relation between the electronic and catalytic properties of solids is due to him.

Subsequently S.Z.Roginskii and F.F.Vol'kenshtein developed the electronic theory of catalysis on semiconductors. Together with O.V.Krylov, they discovered new types of oxidation-reduction catalysts.

S.Z.Roginskii proposed a new classification of catalysts, relating their activity to the nature of the interaction of the catalyst with the substrate. They assigned catalysts to two classes—conductors of the electric current (metals and semiconductors) and non-conducting bodies (ionic crystals and gels). The validity of this classification was tested in relation to many oxidation processes (S.Yu.Elovich, L.Ya.Margolis, and G.M.Zhabrova).

N.I.Kobozev put forward the theory of "active *ensembles*", according to which the active centres of the catalyst are grouped on specific sections of the carrier surface, and developed the mathematics of this theory.

The hypothesis of the important role of adsorbed free radicals in heterogeneous catalysis and of the possibility of catalytic reactions via a chain mechanism was put forward by N.M.Semenov, V.V.Voevodskii, and F.S.Vol'kenshtein.

V.B.Kazanskii investigated by EPR the structure and chemical properties of adsorbed radicals and determined their role in many catalytic processes.

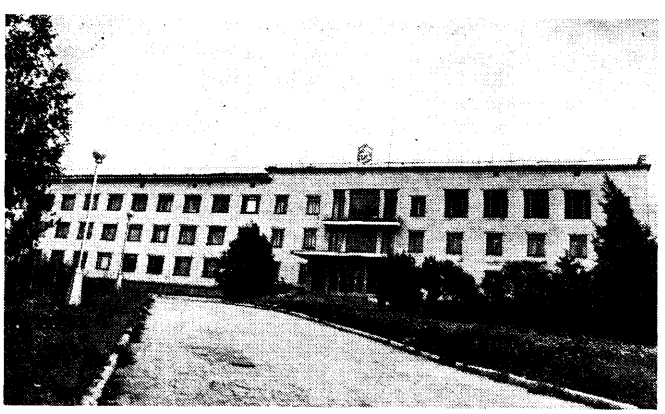


Figure 11. Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.

Studies on the topochemistry of catalysts and of the influence of the phase composition, degree of dispersion, and deformation of the crystal lattice on the properties of catalysts proved to be important (A.M.Rubinshtein, O.M.Poltorak, and A.Ya.Rozovskii).

P.A.Rebinder and E.D.Shchukin developed the principles of the regulation and control of the mechanical strength of catalysts on the basis of the ideas of physicochemical mechanics.

The kinetics and mechanisms of heterogeneous catalytic reactions have been studied (G.K.Boreskov, M.I.Temkin, S.L.Kiperman, V.A.Roiter, Ya.B.Gorokhovatskii, A.I.Gel'bshtein, and G.I.Golodets).

M.I.Temkin developed a theory of the kinetics of reactions on heterogeneous surfaces and the theoretical principles of the industrial synthesis of ammonia and other catalytic processes.

Kinetic isotope methods proved to be effective in studies on the mechanisms of heterogeneous chemical reactions (S.Z.Roginskii and M.B.Neiman).

G.K.Boreskov made a large contribution to the development of catalytic theory and practice. He formulated the principle of the constancy of the specific catalytic activity under the conditions of a constant chemical composition of the catalyst, which has been confirmed for many metallic and oxide catalysts. The concept of the influence of the reaction mixture on the composition and structure of the surface and its catalytic properties and hence on the kinetics of heterogeneous catalytic reactions has been developed. Studies have been made of the scientific basis of the preparation of catalysts, the principles governing the creation of the porous structures of catalysts have been formulated, and new highly efficient catalysts of many processes have been developed and introduced in industry (V.A.Dzis'ko, R.A.Buyanov, V.V.Popovskii, Yu.I.Ermakov, B.I.Popov, and K.G.Ione).

Methods have been developed for the mathematical modelling and automation of catalytic processes designed to reduce the time of laboratory tests (M.G.Slin'ko).

The school of Kazakh chemists founded by D.V.Sokol'skii has been carrying out extensive researches into the liquid-phase hydrogenation of unsaturated compounds (G.D.Zakumbaeva). The electrochemical methods devised by A.N.Frumkin and coworkers are used for the investigation of catalysts and the mechanisms of catalytic reactions.

New types of catalysts of the selective hydrogenation of unsaturated hydrocarbons have been developed under D.V.Sokol'skii's supervision and have been applied in industry for the hydrogenation of vitamins and perfumes and for the elimination of ethylenic hydrocarbons from acetylenic hydrocarbons. Studies on the protection of air from contamination by harmful substances are being carried out.

B.V.Erofeev is developing a ligand field theory of catalysis.

The employment of zeolite catalysts, which promoted an improvement of the output of industrial plant without an increase in factory area and the creation of apparatus with a high unit output, proved extremely effective in many branches of the petrochemical and chemical industry.

Kh.M.Minacheva's studies have made a major contribution to the development of theoretical and practical aspects of catalysis on zeolites. New polyfunctional catalytic systems based on synthetic zeolites have been set up. The catalytic and physicochemical properties of zeolites are being investigated (A.A.Slimkin and A.M.Rubinshtein).

K.V.Topchieva has been investigating the kinetics and mechanisms of a series of heterogeneous catalytic reactions on zeolite and zeolite-containing catalysts—for example, the cracking of hydrocarbons, the transformation of alcohols, and isomerisation. The research into the synthesis, physicochemical properties, and activities of transition metal complexes fixed on a zeolite support is being expanded. Catalysts based on natural zeolites are being investigated by G.V.Tsitsishvili and Kh.I.Areshidze. Catalysts, based on zeolites, for the preparation of hydrocarbon raw material and synthetic liquid fuel from coal, carbon oxides, and hydrogen, are being synthesised. In the presence of ultrahigh-silica zeolites of a new type, C_3–C_4 olefins and olefin-containing industrial petroleum processing gases give rise to a mixture of aliphatic C_6–C_8 hydrocarbons, which constitutes a motor fuel with high octane characteristics (E.D.Radchenko).

The scientific principles of catalytic alkylation on zeolite catalysts have been formulated (V.S.Gutyrya).

Yu.G.Mamedaliev and M.F.Nagiev carried out fundamental studies on petrochemical processes. New highly efficient and selective catalysts have been developed for the manufacture of aromatic nitriles by the oxidative ammonolysis of hydrocarbons: benzonitrile, phthalonitrile, terephthalonitrile, and chlorobenzonitriles (R.G.Rizaev and T.N.Shakhtakhtinskii).

The Ukrainian school of chemists has made a contribution to the development of physicochemical research into catalysis and the training of scientific cadres (V.A.Roiter, K.B.Yatsimirskii, G.I.Golodets, and G.P.Korneichuk). Fundamental studies on catalytic oxidation, whereby one can devise and introduce into practice a series of new catalysts and methods for the purification of gaseous waste, are developing successfully, a classification of oxidation–production reactions has been proposed, and novel gradient-free reactors for the investigation of catalytic reactions have been designed.

Credit is due to Soviet research workers for the development of physicochemical investigations of heterogeneous asymmetric catalysis (E.I.Klabunovskii). Studies are being prosecuted on the synthesis of heterogeneous and metal complex chiral hydrogenation, polymerisation, hydroxylation, and dimerisation catalysts and new promising asymmetric reactions are being sought.

V.M.Gryaznov and V.S.Smirnov are developing a new field of study—catalysis on membranes. The selectivity of many processes, for example, isomerisation, hydrogenation, etc., on membranes are significantly superior to that achieved on previously known catalysts of gas- and liquid-phase reactions. The phenomenon of the coupling of two and more chemical processes on membranes permeable to substances formed in one process and consumed in the other has been discovered. This made it possible to devise a method of synthesising the unsaturated alcohols which are at present obtained from essential oils. Liquid-phase hydrogenation on membrane catalysts is used in the synthesis of pharmaceutical preparations.

The application of quantum chemistry to the solution of problems of catalysis has greatly developed in recent years (V.B.Kazanskii and G.M.Zhidomirov).

Physical research methods are widely used in heterogeneous catalysis (Kh.M.Minachev, V.B.Kazanskii, G.V.Antoshin, and K.I.Zamaraev). Spectroscopic methods are used: EPR, NMR, optical, Mössbauer, X-ray, photoelectron, infrared, and Auger spectroscopy and mass spectrometry. The introduction of new physical methods, such as EXAFS and NMR, in combination with rotation by the magic angle is very promising. Information gained with the aid of these methods permits an approach to the atomic-molecular description of the catalytic step and raises to a higher level the theoretical foundations of catalysis as a whole.

Numerous studies have been carried out in recent years on the creation of new highly efficient catalysts for the most important chemical processes.

New methods have been developed for the dimerisation and oligomerisation of ethylene in the presence of metal complex catalysts as well as procedures for the synthesis of high-purity α-butene and higher linear α-olefins (F.S.D'yachkovskii).

A new mechanism of the catalytic synthesis of methanol from carbon monoxide and hydrogen, which has proved useful for the intensification of the existing process, has been formulated (A.N.Bashkirov).

A new class of catalysts has been created on the basis of the hydrides of transition metal intermetallic compounds, which are highly effective in the hydrogenation, hydroalkylation, and aromatisation of hydrocarbons, the hydrodenitrogenation of nitrogen-containing organic compounds, the hydrogenation of carbon oxides, etc. (V.V.Lunin).

A highly effective chromium-containing olefin hydrogenation catalyst, distinguished by an improved mechanical strength and permitting the synthesis of isoprene with a high selectivity, has been proposed (G.R.Kotel'nikov).
A copper phosphate–zeolite catalyst has been devised for the synthesis of formaldehyde from methanol (K.V.Topchieva and B.V.Romanovskii).

A new highly active ferrite–cobalt catalyst has been developed for the oxidative dehydrogenation of olefinic C_4–C_5 hydrocarbons, whereby it is possible to increase the yield of diene hydrocarbons severalfold in combination with a high process selectivity. A multistage process mechanism has been put forward (R.G.Rizaev).

Studies are being made on the synthesis and testing of active catalysts for the oligomerisation of olefins in order to obtain substitutes for plant oil for use in the paint and varnish industry. A highly efficient synthesis of isoprene from isobutene and formaldehyde has been devised and introduced. The disproportionation of vinyl and allyl halides with formation of the corresponding dihalogenoolefins has been achieved in the presence of a promoted aluminorhenium catalyst (A.N.Bashkirov).

The problem of "kinetics and catalysis" has been for many years the subject of a comprehensive collaboration of the Academies of Sciences of Socialist Countries.

7. Crystal Chemistry

Crystal chemistry in our country originated with the studies of E.S.Fedorov, G.V.Vul'f, A.E.Fersman, and A.V.Shubnikov. The establishment of the Soviet crystal-chemical school is associated primarily with the name of N.V.Belov.

A vigorous development of Soviet crystal chemistry began in the 1930's–1940's mainly at the Moscow scientific centres: the Institute of Crystallography of the USSR Academy of Sciences (IC) (N.V.Belov), the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences (IONKh) (G.B.Bokii and N.V.Ageev), the Karpov Physicochemical Institute (G.S.Zhdanov), and somewhat later the Institute of Organoelemental Compounds (INEOS) A.I.Kitaigorodskii). The Departments of Crystallography, Crystal Chemistry, and X-Ray Diffraction Analysis at Moscow State Univeristy (G.B.Bokii, N.V.Belov, and M.A.Porai-Koshits) and Gorky State University (N.V.Belov) have played an important role both in the development of scientific principles and in the training of qualified cadres of crystal chemists during the 1940's–1950's.

At the present time the structural and crystal-chemical studies have developed widely in many other institutes of the Academy of Sciences of the USSR and the Academies of Sciences of the Union Republics (Moldavian, Latvian, Azerbaijan, Georgian, Uzbek, and Ukrainian), at the Leningrad, Lvov, Kiev, and Kalinin Universities, at the Georgian Polytechnic Institute, and at the Leningrad Technological Institute.

The results of the crystal-chemical research made it possible to create the structural basis for many modern fields of chemistry and to solve many important practical problems.

The scientific and technical revolution in the field of X-ray diffraction analysis of crystals (on the basis of automatic diffractometers and branched sets of programmes for structural calculations on computers) during the 1960's–1970's not only increased sharply the rate, reliability, and accuracy of the investigations but has had a most significant influence on the very content of crystal chemistry as a scientific discipline. The interrelations between crystal chemistry and preparative, physical, and quantum chemistry have become much more varied, the scope of its "incorporation" in chemistry has greatly expanded, the topics dealt in crystal chemistry in which our country has been traditionally strong (the crystal chemistry of intermetallic compounds, silicates, sulphides, and complex and organometallic compounds) have become more varied and have been treated at a deeper level, and certain serious gaps in crystal-chemical research (organoelemental chemistry, structural organic chemistry, bioinorganic chemistry, and bio-organic chemistry) have been rapidly filled. New fields have arisen as well as new aspects of crystal-chemical studies: "energetic" stereochemistry and crystal chemistry—calculations of the stabilities of conformers, of the anisotropy of the interaction of molecules and ions in crystals, and of the energy of the crystal structure; "dynamic" crystal chemistry—the study of atomic vibrations in the crystal lattice; "electronic" crystal chemistry—analysis of the distribution of electron density in the internuclear space in precision X-ray and neutron diffraction studies.

One of the most important fields in Soviet crystal-chemical science—the crystal chemistry of silicates and related mineral and synthetic substances—has been developed by N.V.Belov and his school. Credit is due to Belov for developing the crystal chemistry of silicates with large cations. He also developed the concept of the dynamic role of the SiO_2 molecule in the rearrangement of silicate structures and the segregation of mineral deposits from the cooling magma, which has thrown new light on the processes occurring in the Earth's core. The studies by Belov and his school have made a large contribution to the Earth sciences—mineralogy and geochemistry—and have exerted a wide influence on technology (problems of the setting of cement, the compositions of concretes, etc.).

Studies are being made on oxygen compounds of other classes—lanthanide germanates and silicates, transition metal and lanthanide phosphates, magnesium and calcium borates, molybdates, and tungstates, etc. These studies have contributed to the solution of practical problems of the utilisation of minerals and the development of materials for the new technology. In particular, the crystal-chemical researches into orthophosphates, metaphosphates, and particularly ultraphosphates are related to the problem of synthesising heat-resistant and laser materials, phosphors, and other materials. The analysis of the atomic structures of intermetallic compounds and alloys is being developed. The research by N.S.Kurnakov's students (A.V.Ageev and E.S.Makarov) has made a large contribution to the structural interpretation of phase diagrams, the nature of

constant- and variable-composition phases, etc. Crystal-chemical and crystal-physical studies of intermetallic compounds are being prosecuted (E.I.Gladyshevskii and P.I.Kripyakevich); the structural types of hundreds of intermetallic compounds comprising silicides, borides, aluminides, etc. have been found; a correlation has been traced between the structures and physicochemical properties of substances. The scientific principles of a systematic classification of intermetallic structures with a large variety of variations of isotypical structural elements, both one-dimensional and two-dimensional, are being formulated.

Structural research into semiconductors, in particular sulphides and chalcogenides, is being developed. A systematic crystal-chemical classification of sulpho-salts and sulphide materials has been created (V.V.Bakakin and A.A.Godovikov). A consistent relation between morphotropic transitions and the replacement of semiconducting by metallic properties has been discovered (G.B.Bokii, V.B.Lazarev, and others). Studies are being made on a crystal-chemical basis with a specific search for materials having unusual electrophysical properties (G.S.Zhdanov, Yu.M.Venevtsev, I.R.Rez, and Kh.S.Mamedov), solid electrolytes (L.O.Atovmyan), and organic semiconductors and conductors (R.P.Shibaeva).

The most extensive field of crystal-chemical research concerns coordination compounds. Its foundations were laid by the studies of G.B.Bokii in the 1940's–1950's. Bokii was the first to carry out structural studies on platinum complexes and examined the structural manifestations of the *trans*-influence.

The studies by M.A.Porai-Koshits have made a large contribution to the development of the crystal chemistry and stereochemistry of coordination compounds. He developed the principles of the stereochemistry of Group VIII transition metal complexes as well as molybdenum, tungsten, and lanthanide complexes, established the general characteristics of the stereochemistry of *d* and *f* transition metal thiocyanates, selenocyanates, carboxylates, and mono- and di-amine-complexonates, and formulated the fundamental differences between the structural manifestations of the mutual influence of the ligands in transition and non-transition metal complexes. Structural studies by Porai-Koshits and L.O.Atovmyan of the oxo-complexes of *d* metals in the highest oxidation states have been of great importance. They made it possible to formulate the general rules governing the structures of complexes with multiply linked ligands and to put forward a structural basis for the formation and stable existence of Group V and VI d^{10} metal isopolyanions and heterpolyanions.

The research into cluster and polynuclear compounds has widely developed in recent years (Yu.T.Struchkov). The discovery of the fourth metal–metal bond in d^4 metal compounds has proved of theoretical importance (V.G.Kuznetsov and P.A.Koz'min).

The development of the crystal chemistry of inner-complex compounds was initiated by the studies of E.A.Shugam on the structures of β-diketonates and salicylideneaminates. The crystal chemistry of carboxylates, dienes, thiosemicarbazones, and other related inner complexes of copper, cobalt, and iridium is being elucidated (T.I.Malinovskii). The crystal chemistry of substituted *d* and *f* metal benzoates and thiobenzoates is being studied (Kh.S.Mamedov). Crystal-chemical investigations are being made on biocomplex compounds, mainly complexes of metallic bioelements with bioactive ligands (G.V.Tsintsadze and A.E.Shvelashvili). The results of the research in this field are significant for the specific search for compounds with optimum biological activity.

A large series of uranyl compounds with different ligands have been investigated (Yu.N.Mikhailov). These studies established the characteristics of the associative interactions of the coordination polyhedra of uranyl and led to the discovery of the relation between the stoichiometry and the structure of the crystal.

Certain new fields in coordination crystal chemistry, namely those of *d* and *f* metal metaphosphimates, metallocarbaboranes, and complexes with branched polymetallic chains, have developed in recent years (M.A.Porai-Koshits and Yu.T.Struchkov).

The crystal chemistry of organometallic, organoelemental, and organic compounds is developing vigorously. Studies are being made on transition metal π-complexes and carbonyls—the products of the fixation of small molecules many of which have proved promising in catalysis. Data on the steric disposition of the functional groups in such complexes made it possible to refine the mechanisms of many catalytic processes and to control effectively their course.

Research is being prosecuted into boron-, silicon-, phosphorus-, arsenic-, antimony-, tellurium-, sulphur-, selenium-, and fluorine-containing organoelemental compounds of different classes, including compounds such as carbaboranes and elementocarbaboranes, polyorganosiloxanes, silatranes, silacyclobutanes, phosphorylated sugars, etc. Even more varied classes of organic compounds have been investigated, including photochromic and thermochromic compounds, optically active aziridine and isoquinazolidine derivatives, organic semiconductors and conductors, and polycyclic and skeletal compounds (Yu.T.Struchkov, L.O.Atovmyan, J.Bleidelis, R.P.Shibaeva, and L.G.Vorontsova).

Increased attention has been devoted to biologically active organic compounds of different types: diazo-compounds, organophosphorus compounds, aminoacids and their analogues, and psychotropic, antitumour and antitubercular preparations.

The Soviet Union has priority in the development of theoretical organic crystal chemistry. Its foundations were laid in the 1950's by A.I.Kitaigorodskii. The present stage of research in this field (A.I.Kitaigorodskii and P.M.Zorkii) is characterised by a combination of the geometrical and energetic approaches. Methods have been developed for the direct calculation of the intermolecular interaction energy on the basis of the empirical method of atom–atom potentials. The characteristics and conditions of the formation of organic solid solutions and ordered heteromolecular compounds have been studied (A.I.Kitaigorodskii). A new approach to the interpretation of organic structures has been developed—a method based on the symmetry of the potential function, and made it possible to justify theoretically the statistics of the distribution of structures among Fedorov groups. A systematic classification of organic structures has been established on this basis. The phenomenon of supersymmetry in the crystals of molecular compounds has been observed (P.M.Zorkii).

8. High-Energy Chemistry

High-energy chemistry deals with the study of the kinetics and mechanisms of chemical reactions characterised by a high concentration (in excess of the equilibrium value) of species (electrons, ions, free radicals, and excited molecules and atoms), which have an excess energy exceeding the energy of thermal motion and frequently also the energy of the chemical bonds. This branch of physical chemistry includes radiation chemistry, plasmachemistry, photochemistry, and

laser chemistry. It also includes studies on the chemical and physicochemical reactions in condensed media under the influence of shock waves, the study of reactions in molecular beams, and many fields of nuclear chemistry (for example, the chemistry of new atoms, in particular positronium and muonium).

Radiation chemistry. The first radiation-chemical studies in our country were carried out even before the Great October Socialist Revolution. N.A.Orlov and N.D.Zelinskii investigated processes occurring in organic compounds under the influence of ionising radiation and observed, in particular, the occurrence of degradation and polymerisation processes. A series of interesting results were obtained in the 1920's–1930's, including the determination of the sensitising effect of the surfaces of solids on radiation-chemical processes (L.V.Pisarzhevskii) and the measurement of the radiation-chemical yield of tervalent iron in the iron(II) sulphate dosimetric system (N.A.Shishkov).

Systematic studies in the field of radiation chemistry were begun in the Soviet Union towards the end of the 1940's and the beginning of the 1950's in connection with the vigorous development of the practical utilisation of atomic energy. In 1946 A.N.Frumkin, G.V.Akimov, P.A.Rebinder, N.A.Bakh, S.S.Medvedev, V.L.Karpov, and M.A.Proskurnin set up the first specialist radiation-chemical laboratories and groups. At the present time the research in this field of physical chemistry is being carried on in many scientific and higher educational establishments of the USSR.

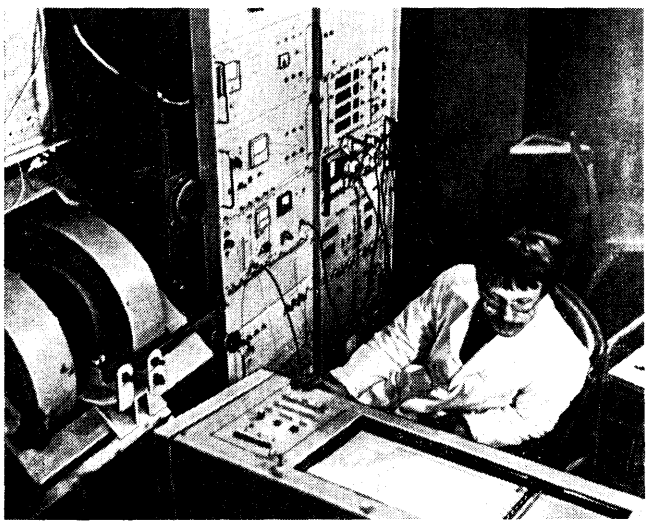


Figure 12. Electron spin echo spectrometer (Institute of Chemical Kinetics and Combustion of the Siberian Division of the USSR Academy of Sciences).

Soviet scientists have made a considerable contribution to each branch of radiation chemistry, starting with the development of the theoretical principles of the creation of the radiation-chemical technology. They achieved significant advances in the study of ion–molecule reactions, the transfer of energy in radiolysis, the radiolysis of water, aqueous solutions, and organic compounds, the radiation modification of polymers, radiation polymerisation, the dosimetry of ionising radiation, and the development and introduction of new radiation-chemical technological processes. One is fully justified in concluding that radiation chemistry in the USSR is fully up to the level of any advances in this field anywhere in the world.

The elementary radiation-chemical gas-phase processes have been studied mass-spectrometrically. The ionisation of simple and complex molecules by electron and photon impact, the formation of negative ions on electron impact, and the ionisation of molecules in collisions with highly excited neutral atoms and molecules have been studied. Ion–molecule reactions in gaseous organic substances have been discovered in the USSR (V.L.Tal'roze and E.L.Frankevich). The method of photoelectron spectroscopy, devised in our country, is important for research in this field (F.I.Vilesov).

The formation and properties of free radicals in various irradiated solid systems at low temperatures have been investigated in detail with an extensive use of the EPR method. The steric distribution of free radicals has been determined by the spin echo method and the structures of traps for captured electrons in many irradiated systems have been established (Yu.D.Tsvetkov). The method of pulse radiolysis has been used successfully in recent years for the investigation of short-lived species in solids. Fig.13 presents the absorption spectra of short-lived (half-life ~1 μs) species (A.K.Pikaev and V.N.Shubin). Soviet scientists investigated the characteristics of the radiothermoluminescence of irradiated solids. In particular, it has been observed that radiothermoluminescence peaks occur at the phase transition points (N.Ya.Buben and V.G.Nikol'skii). The photochemical reactions of free radicals in irradiated systems have been studied in detail. The non-additivity of the joint action of radiation and light has been discovered (S.Ya.Pshezhetskii and V.K.Milinchuk).

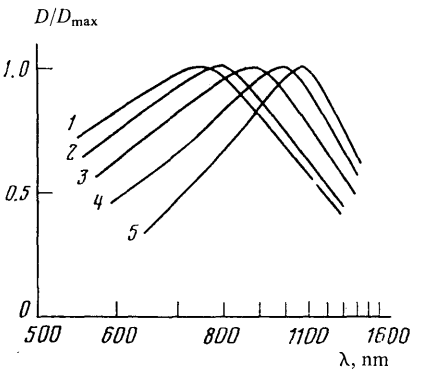


Figure 13. Optical absorption spectra of short-lived solvated electrons in NaCl (curve *1*) and KCl (curve 5) melts and in NaCl + KCl mixtures of different compositions (mole %) [2) 80 + 20; 3) 50 + 50; 4) 20 + 80] at 1070 K measured by pulse radiolysis; D = optical density of the melt.

A detailed study has been made of the nature of the solvated electrons arising on radiolysis. The formation of stable solvated electrons has been observed in the low-temperature radiolysis of aqueous solutions of alkalis (V.I.Spitsyn, A.K.Pikaev, and B.G.Ershov). Short-lived solvated electrons have been investigated in irradiated

aqueous solutions of alkalis, alcohols, liquid ammonia, hydrocarbons, melts of alkali metal halide compounds, and in crystalline ice (N.A.Bakh, P.I.Dolin, A.K.Pikaev, A.V.Vannikov, and others). Important results have been obtained in the study of electron tunnelling in irradiated solid systems (V.I.Gol'danskii, K.I.Zamaraev, and B.G.Ershov).

The radiation chemistry of aqueous systems constitutes the most thoroughly investigated branch of radiation chemistry owing to the wide-scale employment of water and aqueous solutions in the technology of the processing of irradiated nuclear fuel and reactor construction. The studies of P.I.Dolin, B.V.Ershler, V.I.Veselovskii, M.A.Proskurnin, N.A.Bakh, and A.K.Pikaev led to the determination of the radical mechanism of the radiolysis of water. The characteristics of the radiolytic reactions in multicomponent aqueous and aqueous organic systems, including extractants and diluents (V.I.Medvedovskii and G.F.Egorov) and aqueous solutions of uranium and transuranic elements (A.K.Pikaev and M.V.Vladimirova), have been determined in recent years. A radiation-chemical method of synthesis of heptavalent neptunium, plutonium, and americium has been proposed and developed (V.I.Spitsyn, A.K.Pikaev, and N.N.Krot).

Studies on the radiation-chemical reactions in solid and liquid organic compounds have been carried out by N.A.Bakh, Kh.S.Bagdasar'yan, L.S.Polak, V.L.Tal'roze, M.A.Proskurnin, V.B.Saraeva, and others. The initial stages of the radiation-chemical oxidation of hydrocarbons and the hydroxymethylation of organic compounds, the mechanism of the radiolysis of alcohols over a wide temperature range, and radiolytic processes in aqueous solutions of many organic substances (including biologically important substances) have been studied.

Considerable advances have been made in the field of the radiation chemistry of polymers. The radiation-induced cross-linking of polyethylene has been discovered (V.L.Karpov and V.A.Kargin), the track effects in the irradiation of polymers have been studied (A.M.Kabakchi and Ya.I.Lavrentovich), the characteristics of the radiation-induced ionic graft polymerisation have been elucidated (V.Ya.Kabanov and V.I.Spitsyn), the gas-phase radiation-induced graft polymerisation has been developed (B.L.Tsetslin), a method has been proposed for improving the quality of wood by impregnating it with monomers and subsequent polymerisation under the influence of gamma-radiation (V.L.Karpov), and ultralow friction has been noted after the radiation treatment of the surfaces of solid, including polymeric, bodies (V.L.Tal'roze).

Theoretical studies served as a basis for the intensive development of applied radiation chemistry. During the last 15–20 years, studies on radiation-chemical technology have been carried out along the following main lines: (1) radiation-induced modification of materials (mainly polymeric materials) in order to improve their operating properties and to simplify the technology of their manufacture; (2) radiation polymerisation and copolymerisation (including graft polymerisation); (3) preparation of composite materials (wood-plastic, concrete-polymer, and other porous materials, raidation-induced hardening of paint and varnish coatings, etc.); (4) radiation-chemical synthesis based on chain processes; (5) practical application of the radiation-chemical technology to ecological problems (radiation water treatment and radiation purification of waste water and gaseous waste).

In all the above fields, significant advances have been made. Radiation-chemical sulphochlorination (R.V.Dzhagatspanyan) and telomerisation (P.A.Zagorets and A.A.Beer), the manufacture of cable with radiation-modified insulation (E.E.Finkel'), radiation-chemical vulcanisation of thermostable self-adhesive electrically insulating tape and rubber-glass fabric (S.V.Aver'yanov, I.Ya.Poddubnyi, and others), radiation-induced hardening of paint and varnish coatings on the wooden cabinets of television and radio sets (F.Z.Raichuk, G.V.Shiryaeva, and others), and the radiation technology of the modification of textile fibres (B.L.Tsetslin, V.D.Orekhov, and others) have been introduced into industry. Experimental industrial tests are being made of many other radiation-chemical processes: the synthesis of dibutyltin dibromide, the preparation of parquet blocks from modified birchwood, radiation-flotation elimination of mercury from waste water, and others.

The advances in applied radiation chemistry are to a large extent determined by the high level of research and development in the field of radiation apparatus engineering, to the development of which Soviet scientists have made a large contribution (A.Kh.Breger, Yu.D.Kozlov, and others). In recent years the scientific foundations were created for a combined electrical power-radiation utilisation of nuclear reactors involving the simultaneous generation of heat (and/or electrical energy) and γ-radiation for radiation-chemical production (A.Kh.Breger and others). A quantitative basis of the theoretical and applied radiation chemistry, namely ionising radiation dosimetry, has been developed (S.V.Starodubtsev, V.V.Generalov, A.M.Kabakchi, and A.K.Pikaev). New dosimetric systems (dichromate and glucose solutions, polymer films, etc.), suitable for the determination of absorbed doses in various ranges, have been proposed.

Plasmachemistry. Plasmachemistry has been formulated as an independent discipline at the beginning of the 1960's. The scientific foundations of plasmachemistry were created and its general postulates and experimental and computational methods were elaborated (L.S.Polak). This led to procedures for the wide-scale investigation of specific plasmachemical processes and their industrial realisation. Three main fields of plasmachemistry, whose development is interdependent, arose as a result: theoretical plasmachemistry, applied plasmachemistry, and scientific principles of plasmachemical technology and apparatus engineering (M.F.Zhukov, V.D.Parkhomenko, T.N.Miller, N.N.Rykalin, V.N.Troitskii, and S.N.Shorin).

The fundamental ideas and methods of non-equilibrium chemical kinetics were first formulated in theoretical plasmachemistry (L.S.Polak). Non-equilibrium chemical kinetics altered not only the character of the approach to the analysis of chemical reactions but the very object of study, which has come to consist of molecules in a specific quantum state. The necessity for the joint consideration of physical (in particular relaxation) channels and chemical reaction channels led to the development of appropriate mathematical models, new experimental methods, and methods for the interpretation of experimental data.

The application of computers to the solution of the systems of fundamental equations of non-equilibrium chemical kinetics and the development of spectroscopic, probe, ultrahigh frequency, and corpuscular diagnostic methods for reacting non-equilibrium systems (in particular and especially plasmachemical systems) made it possible to elucidate for the first time the characteristics of the kinetics and mechanisms of the physicochemical processes in such systems (A.A.Ovsyannikov, V.D.Rusanov, and D.I.Slovetskii). Diatomic and triatomic molecules were studied: H_2, O_2, N_2, CO, SiO, CO_2, H_2O, SiO_2, etc., as well as certain more complex molecules: CH_4, NH_3, CF_4, etc. The kinetics and mechanisms of reactions

involving species in a vibrationally excited ground electronic state and an electronically excited state were studied, the contributions of electron impact, metastable states, $V-V$ and $V-RT$ exchange, and predissociation to these processes were demonstrated, and the internal relation between dissociation-recombination and vibrational relaxation (L.S.Polak and D.I.Slovetskii) and plasma-beam processes were investigated (A.A.Ivanov).

Numerous studies, devoted to the determination of the form of the distribution functions for reactants and reaction products with respect to energy and the elucidation of the influence of these functions on the rates of specific chemical reactions have been carried out. In the case of reduced-pressure electric discharges, it was possible to find for the first time the dependence of this function on the parameters of the electric field, the degree of ionisation, and pressure (L.S.Polak, Yu.A.Ivanov, and Yu.A.Lebedev).

Detailed experimental study and mathematical modelling of plasmachemical non-equilibrium and quasi-equilibrium processes made it possible to develop a series of plasmachemical processes characterised by short contact times ($\sim 10^{-4}$–10^{-1} s), a high sensitivity. a high degree of reaction, the possibility of processing raw materials normally difficult to process, and purity.

Approximately 200 plasmachemical processes have been applied industrially in the USSR in the electronic, radio-engineering, electrotechnical, instrumental, automobile, glass, and other branches of industry and ferrous and non-ferrous metallurgy.

A set of unique processes have been devised in the manufacture of integrated microcircuits, including the deposition of thin films in a non-equilibrium glow discharge (including polymer films), accelerated etching of dielectric and semiconducting materials in a fluorocarbon plasma, and final polishing; in addition, plasmachemical methods are used to obtain abrasive powders in a high-frequency plasma and in a number of other processes which cannot be achieved by other chemical methods at the present time.

Ultradisperse powders of refractory metals and oxides and mutual solid solutions and compositions based on transition metals nitrides, boride nitrides, and carbide nitrides, as well as metal carbides are obtained with the aid of plasma-chemical methods. Instruments (cutting tools, drills, and machine components, etc.) are strengthened with the aid of titanium nitride obtained in a high-frequency plasma, the surfaces of metallic, glass, and quartz articles are modified, nitrogenation and siliconation are carried out, the surface of polyethylene is treated, and plasmachemical polymerisation is carried out.

A technology of the preparation of ferrites and certain catalysts has been set up as well as a technology of the formation of various types of anticorrosion, strengthening, conducting, protecting, optically transparent, and other coatings.

Experimental industrial tests of highly efficient waste-free large-scale plasmachemical processes, modified for industrial application, have been successfully completed: the synthesis of acetylene, ethylene, and technical hydrogen by the pyrolysis of natural gas and petroleum fractions (including heavy fractions); the preparation of synthesis gas for the formation of vinyl chloride; the binding of atmospheric nitrogen into nitric oxide and the formation of complex nitrogen—phosphorus fertilizers; the synthesis of HCN; the processing of waste from organochlorine industries; the formation of titanium dioxide; the formation of technical carbon.

The important role played by low-inertia plasmachemical processes in the development of the power engineering of the future, in particular the atomic-hydrogen power engineering as well as their possible role as regulators of the load in power systems should be noted.

The industrial realisation of plasmachemical processes required the creation and development of the scientific principles of the plasmachemical technology and apparatus construction. The characteristics of the "pumping" of various types of energy into a multicomponent reacting system and the mechanisms of its conversion into the energy of the excited and ionised species with a high reactivity have been elucidated. For reactions in mixing turbulent plasma fluxes, the influence of the degree of turbulence and of its time variation on the rate and selectivity of chemical reactions was demonstrated for the first time. The mutually correlated pulsations of temperature (energy) and concentration in turbulent reacting mixtures with phase transformations have been investigated; the simplest similarity criteria, permitting the transition from a laboratory scheme to industrial technology, have been formulated. The influence of factors such as the characteristics of the mixer, the quenching device, heat and mass transfer, the application of external electric, magnetic, and electromagnetic fields as well as the effect of the beamed flux of charged particles on the organisation of the plasmachemical technology has been elucidated.

Photochemistry. The study of chemical reactions occurring under the influence of light is important for the theory of chemical processes and for the solution of the problems of photosynthesis, photoreception, photography, and light stabilisation of polymeric materials.

P.P.Lazarev was the first to investigate the photodecolorisation of dyes.

Fundamental photochemical studies have been carried out by A.N.Terenin. His theory of the triplet nature of the metastable states of organic molecules responsible for their phosphorescence has received numerous experimental confirmations. The properties of triplet states have been investigated and their role in various photochemical and photophysical processes has been discovered. The phenomenon of the triplet–triplet energy transfer has been demonstrated (A.N.Terenin and V.L.Ermolaev).

Using the method of flash photolysis, A.V.Karyakin and A.K.Chibisov demonstrated the important role of the triplet state in photochemical oxidation-reduction reactions with participation of pigment and dye molecules.

V.N.Kondrat'ev initiated the study of the elementary step in the interaction of light with matter. The mechanism of the induced predissociation and energy transfer processes has been studied.

Kh.S.Bagdasar'yan demonstrated the occurrence of two-quantum reactions—a fundamentally new type of photochemical reactions, which occur as a result of the absorption of a light quantum by a molecule which is already excited and is in the triplet state. The reactions of the highly excited molecules formed, namely ionisation with formation of a "captured" electron, sensitised decomposition of the solvent, etc., have been investigated.

The characteristics of these reactions, for example, the exponential dependence of the quantum yield of the overall process (sensitisation plus ionisation) on the energy of the highest excited state, have been discovered. Two-quantum reactions involving the participation of singlet states have also been found and studied. N.V.Fok, M.V.Alfimov, and V.E.Kholmogorov also investigated two-quantum reactions.

The phenomenon of triplet–triplet energy transfer from highly excited donor molecules to unexcited acceptor molecules has been observed. It has been shown that the phenomenon is due to the exchange-resonance interaction between the energy donor and acceptor and that its efficiency

increases with increase of the energy of the highly excited triplet state of the donor. As a result of the transfer of large amounts of the electronic excitation energy (5–6 eV) to the acceptor, the latter undergoes various chemical transformations (dissociation, *cis–trans* isomerisation) (M.V.Alfimov).

The influence of the magnetic field on photophysical and photochemical processes in the gas phase has been studied and it has been observed that the magnetic field quenches the fluorescence of deuteroformaldehyde and SO_2 by 40–50%. The magnetic field accelerates the photodecomposition of deuteroformaldehyde and decreases the rate of reaction of SO_2 molecules in the triplet state with titanium. It has been established that the influence of the magnetic field on photochemical reactions is due to the mixing of different states of the molecule and changes in the distances between the energy levels of the reactants (Yu.N.Molin).

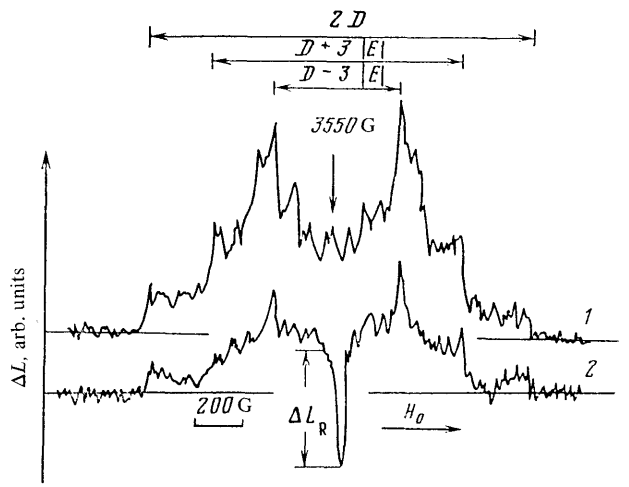


Figure 14. Magnetic resonance spectra of short-lived pairs of paramagnetic species in polycrystalline specimens of anthracene complexes. The spectra were detected from measurements of ΔL for the slow fluorescence of the specimen due to the reactions in the pairs of species: 1) non-irradiated specimen—the spectrum corresponds to pairs of triplet anthracene excitons (10^4 pairs per specimen); 2) the same specimen irradiated with a dose of 0.3 Mrad. The central ΔL_R line of the spectrum is due to the absorption of the ultrahigh frequency power by the radicals in the triplet exciton–radical pairs; D and E are the fine splitting factors of the excited triplet states of anthracene.

It has been shown that the rates of reactions involving the intermediate formation of a pair of paramagnetic species, for example, radical-ions, depend on the state (singlet or triplet) in which this pair exists. The achievement of the magnetic-resonance modulation of the rates of photochemical reactions and the discovery of the method of recording the EPR of short-lived ($\tau \sim 10^{-9}$ s) radical pairs when their number in the specimen is only 10^3–10^5 were developments of the above investigations (Fig.14). The method is used nowadays to investigate the mechanisms of reactions excited by light in molecular solids, in solutions, and in biological systems (E.L.Frankevich and A.I.Pristupa).

The development of modern pulse methods permitted the study of extremely rapid (over a period as short as 10^{-12} s) photoprocesses, which is of fundamental importance for the investigation of the mechanisms of elementary reactions. The spectra of short-lived products formed on excitation of thioindigo over periods in the range 4×10^{-9}–7×10^{-12} s have been investigated. The results obtained require the revision of the existing ideas about the mechanism of the *cis–trans* isomerisation of these dyes (M.V.Alfimov).

The mechanisms of the photochemical reactions of a series of dyes in solutions have been investigated. Ways of inhibiting photochemical reactions leading to irreversible transformations in the dyes have been found and it has been established that the quenching of the triplet states of xanthene dyes by inorganic ions proceeds via mechanisms involving electron and energy transfer. An approach has been developed to the quantitative estimation of the contribution of each of these processes to the overall quenching effect. A correlation has been discovered between the efficiency of the quenching of triplet states and the free energy of the reaction (A.K.Chibisov).

The detailed mechanisms of the photochemical reactions between the excited states of complex organic molecules and free radicals (nitroxy-radicals, phenoxy-radicals, semiquinone radicals, and other aromatic radicals) have been established. The occurrence of the elementary reaction involving the acceleration of the intersystem crossing from the excited singlet to the triplet state on interaction with radicals has been demonstrated by flash photolysis. The sequence of the elementary reactions in the quenching of the triplet states of complex organic molecules (aromatic hydrocarbons, dyes, and related compounds) by free radicals, electron donors and acceptors, and hydrogen atoms has been determined. The spectroscopic-kinetic characteristics of short-lived triplet exciplexes have been obtained and their important role as intermediates in photochemical electron transfer reactions has been established (V.A.Kuzmin).

The photoionisation processes involving molecules in the gas phase and in condensed states have been investigated and extensive information has been obtained about the mechanisms of the interaction of ultraviolet radiation with matter and about the electronic structures of the compounds studied (F.I.Vilesov and M.E.Akopyan). The processes occurring on the surfaces of semiconductors with participation of organic sensitiser molecules have been studied by I.A.Akimov. The mechanism of the photochemical oxidation of hydrocarbons sensitised by mercury vapour and chlorine has also been investigated (A.B.Nalbandyan). Studies have been made on reactions involving photosubstitution in aromatic compounds and the photoreduction reactions of aromatic nitro-compounds (A.V.El'tsov). Photochemical processes in liquid and solid solutions of anthracene compounds have been studied in detail by A.S.Cherkasov.

A new view on the tautomerism of aromatic compounds with an intramolecular hydrogen bond in the ground and electronically excited states has been justified. A new interpretation of the anomalous shift of the fluorescence wave length and of the changes in the parameters of photochromism and solvatochromism has been based on the ideas developed (D.N.Shigorin and R.N.Nurmukhametov).

A theory of the photoinitiated recombination of radicals, based on the tunnel mechanism of the transfer of hydrogen atoms, has been developed and agrees well with the experimental data for the recombination of radicals in many irradiated compounds (ammonia and ethanol).

A theory of the absorption of photons in a triplet collision of an electron, a photon, and an atom as an elementary step in a photoradiation process has been devised and general

expressions have been obtained for the cross-section of the triplet collision. The mechanism of the photoradiation processes based on the stepwise excitation of molecules by electron impact and a light quantum and on the excitation of the captured electrons have been established. These ideas have been confirmed experimentally (S.Ya.Pshezhetskii).

A comprehensive experimental and theoretical basis has been provided for a new field of radiation chemistry and photochemistry—that of photoradiation processes in which the rates and directions of the physicochemical processes occurring in the specimen under the influence of ionising radiation are altered significantly as a result of the simultaneous irradiation of the specimen by light which is not absorbed by the initial substance (S.Ya.Pshezhetskii, V.K.Milinchuk, and E.R.Klinshpont).

A series of investigations of electron and proton phototransfer reactions and the heterolytic photodissociation and photosubstitution of excited complexes (exciplexes) and of their role in photoprocesses have been carried out and the nature and the kinetics of the reactions of organic molecules in excited electronic states have been determined. It has been suggested that induced electronic excitation energy degradation processes occur in the elementary step, compete with the photochemical reactions, and limit their quantum yield. The principle of lasers based on adiabatic photochemical reactions was proposed for the first time and was later used in photodissociation, exciplex, and certain liquid retunable lasers. The possibility of the tunnel electron phototransfer over distances up to 10 Å has been demonstrated (M.G.Kuz'min).

The kinetics and mechanisms of photochemical reactions in the solid phase have been studied at low temperatures (down to 77 K). Homolytic and molecular decomposition reactions, stereoisomerisation and valence isomerisation, and ligand exchange in complexes have been studied. A relation has been established between the efficiency and direction of the reaction and the nature of the migration of the molecules and molecular fragments. A function whereby one can estimate the efficiency of the homolytic photodecomposition reaction as a function of the properties of the decomposing molecule, the matrix, and the photon energy has been proposed on the basis of the free volume model. In photochemical reactions where there is a distribution of molecules with respect to their reactivities, a change has been observed in the nature of this distribution as a result of the dissipation of the energy of the photochemically inactive photons (V.S.Gurman).

The kinetics and mechanisms of photochemical reactions of free radicals of various types have been studied and their efficiencies have been characterised quantitatively. The phenomenon of the free radical-stimulated photodegradation of the main chain of carbochain macromolecules has been observed for solid polymers. It has been established that the ageing of poly(ethylene oxide) and aliphatic polyurethanes takes place mainly as a result of photochemical reactions of macroradicals. It has been shown that the ratio of the efficiencies of the degradation and cross-linking processes in polymers is determined by the temperature and spectral composition of the irradiating light (N.V.Fok and M.Ya.Mel'nikov).

It has been shown that the mechanism of the photochemical oxidation of various polymers under the influence of sunlight is based on radical-chain reactions and that the source of photoinitiation can be both peroxides and non-peroxide products. Photochemical oxidation with participation of singlet oxygen is not important even for polydienes containing reactive double bonds in each unit. It has been shown that at $T \ll T_{st}$ there is a distinct kinetic non-equivalence of the reacting low-molecular-weight substances and macromolecules in photochemical reactions. A relation has been found between the efficiency of low-molecular-weight sensitisers and the rate of migration of the free valence in a polymer matrix. The mechanism of the action of a series of light sensitisers has been established and a theory of the synergistic action of mixtures of stabilisers, protecting polymers from the effects of light, has been developed. Fig.15 shows that the theory makes it possible, in particular, to describe the experimental dependence of the photochemical oxidation inductive period and the composition of the mixture of stabilisers (u.v. absorber and antioxidant). The theory created a scientific basis for a selection of effective compositions of light stabilisers (V.Ya.Shlyapintokh and O.N.Karpukhin).

The characteristic features of the photochemical transformation of polymers under the influence of vacuum ultraviolet light have been determined: the occurrence of photochemical processes in very thin (~0.1 μm) surface layers; the "etching" of the surface as a result of the high density of the absorbed energy; high quantum yields of the main products exceeding by 2–3 orders of magnitude the quantum yield of the photolysis due to softer ultraviolet light; a much higher than in radiolysis contribution of molecular processes compared with radical processes (V.E.Skurak).

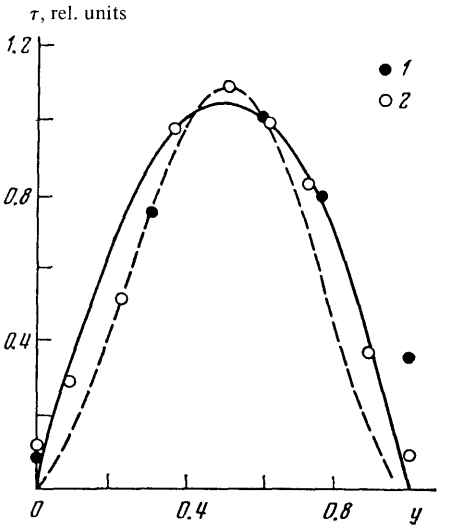


Figure 15. Dependence of the induction period in the photochemical oxidation of polybutadiene (1) and polychloroprene (2) on the fraction of the antioxidant y in the antioxidant–u.v. absorber mixture; u.v. absorber–benzophenone; antioxidant–ionol (1) and bisphenol 2246 (2). Curves—calculation; circles—experimental data for different oxidation conditions.

The polymerisation of cyclic olefins with ring opening under the influence of ultraviolet radiation in the presence of tungsten halides (without the addition of the organometallic component) has been observed and investigated.

The characteristic features of the movement of molecules in the course of the anisotropic chain growth in photocyclopolymerisation reactions of crystalline monomers have been investigated and it has been shown that the degree of anisotropy of the polymer chain is independent of the reaction temperature. A scheme explaining the directional movement of monomer molecules to the active centre has been elaborated (A.D.Abkin).

Studies on the modelling of various photobiological processes and photochemical reactions of biologically important molecules constitute a vigorously developing field. A.A.Krasnovskii and coworkers observed and investigated the ability of light-excited molecules of chlorophyll and its analogues and derivatives to undergo reversible reduction and reverse oxidation. A new class of photochemical reactions of chlorophyll and its analogues, namely reversible photochemical reduction, which has come to be called in the literature the "Krasnovskii reaction", was discovered.

The ability of excited chlorophyll and its analogues to effect the photosensitised electron (hydrogen) transfer has been established.

The elementary photochemical processes with participation of the molecules of photosynthetic pigments and other metal-containing porphyrin compounds have been investigated by A.A.Krasnovskii, A.K.Chibisov, G.P.Gurinovich, A.N.Savchenko, K.N.Solov'ev, and I.I.Dilung.

The ability of aqueous suspensions of TiO_2, ZnO, WO_3, CdS, and other inorganic photocatalyst-semiconductors to effect the photosensitised formation of oxygen and hydrogen has been discovered (A.A.Krasnovskii).

Studies are being prosecuted on the chemical modelling of natural photosynthesis in order to devise transformers of solar energy into the potential energy of fuels. A chemical model of bacterial photosynthesis has been proposed and it has been shown that in the reaction photosensitised by synthetic dyes there is a possibility of the reduction of the protons of the medium to molecular hydrogen under the influence of chemical electron donors. A chemical system involving oxygen in the course of the photocatalytic oxidation of water by electron acceptors has been studied. A chemical model of the photosystem II in plant photosynthesis has been devised (A.E.Shilov).

The mechanism of the action of promising homogeneous photocatalysts of the evolution of hydrogen from water, whose activity approaches that of enzymes of the type of hydrogenases, has been formulated and investigated. These catalysts include certain polynuclear transition metal compounds, which can be regarded as synthetic analogues of the active centres of hydrogenases. The ability of transition metal complexes to function as effective homogeneous catalysts of the evolution of oxygen from water has been observed and is being investigated. Using porphyrin photocatalysts, it has been possible to achieve the phototransfer of electrons through lipid membranes with an appreciable quantum yield and to investigate the mechanism of this process (K.I.Zamaraev).

The mechanism of the decomposition of water photosensitised by phthalocyanine, as a result of which hydrogen is obtained, has been studied (V.E.Kholmogorov).

Studies on the modelling of photosynthesis using photoelectrochemical systems are developing; a mechanism has been proposed for the primary stages of photosynthesis. the essential feature of which reduces to a kind of photoelectrolysis of water in the chloroplast (G.G.Komissarov).

Studies are being made on the physicochemical properties of chlorophyll-containing model systems: adsorption layers, monolayers at interfaces between phases, surfactant micelles, and polymer matrices (L.I.Nekrasov).

Ideas concerning the decisive role of vibronic interactions and the accompanying conformational rearrangements of the macromolecular components in complexes of synthetic reaction centres have been developed on the basis of studies of electron transfer in the simplest protein-chromophore complexes isolated from plants. It has been shown that the electron transfer is coupled with conformational rearrangements and polarisation of the protein molecule of the reaction centre (A.B.Rubin and A.K.Chibisov).

It was shown for the first time that the primary conversion of solar energy in the chlorophyll of photosynthesising organisms takes place over a period of the order of picoseconds, i.e. is much faster than the physical energy scattering processes. The high quantum efficiency (80–90%) of the utilisation of photons in photosynthesis, which corresponds to the energy efficiency of a photoelectrochemical chemical process, amounting to ~10%, has been demonstrated experimentally (A.Yu.Borisov).

In studies on the visual pigment (rhodopsin), new data have been obtained concerning the kinetics of its conversion in the forward and reverse photochemical reactions. The generation of a photoelectric potential on the photoreceptor membrane of the visual cell has been observed and the rate of this process has been measured. In the study of the mechanisms of the damaging effect of light on vision, it was established that retinal, the chromophoric group of rhodopsin, can act as a photosensitiser of the oxidation of the principal molecular components of the photoreceptor membrane (rhodopsin and lipids) in the final stages of the photolysis of rhodopsin. It has been shown that antioxidants can be regarded as promising photoprotectors of the organs of vision. These investigations are important for the understanding of the primary mechanisms of vision and for the elucidation of the pathogenesis of several diseases of the eyes (M.A.Ostrovskii).

Photoinduced free-radical processes with participation of proteins are being investigated (L.P.Kayushin).

The wide-scale application of photochromic compounds in technology has been stimulated by the vigorous research into their properties and the mechanism of photochromism (V.A.Barachevskii, M.A.Gal'bershtam, V.A.Kuz'min, and D.A.Topchiev). The synthesis of new photochromic compounds based on spiropyrans, which absorb visible light is being studied (V.I.Minkin, E.R.Zakhs, and L.S.Efros),

The studies of K.V.Chibisov have been devoted to the photochemical principles of photographic processes; he discovered the nature of photographic sensitivity and investigated the mechanism of the chemical sensitisation of photographic emulsions.

New effective spectral sensitisers belonging to the class of polymethine dyes have been obtained for various photographic materials and introduced into industry (I.I.Levkoev and A.I.Kiprianov).

A method for the formation of line and half-tone photographic images on silver halide emulsions with the aid of non-silver physical development in the presence of an amount of silver smaller than usual by a factor of 10–100 has been devised on the basis of Kh.S.Bagdasar'yan's theory of physical development.

Studies on the formation of non-silver light-sensitive enzyme materials have been continued. M.V.Alfimov observed and investigated the phenomenon of the acceleration of the crystallisation of finely dispersed particles of organic compounds on irradiation with ultraviolet light. He established that, for amorphous particles of *cis*-arylethylenes, this phenomenon is determined by the induction of the crystallisation of the particles by the molecules of the *trans*-isomer formed as a result of the *cis–trans* photoionisation reaction. It was shown experimentally on model systems that the phenomenon of the photoinitiated crystallisation serve as the basis of the action of highly sensitive non-silver photographic materials.

The scientific principles of luminescence photography have been developed; the possibility of creating luminescent photographic materials with a high sensitivity and resolving power has been demonstrated theoretically and experimentally. Laboratory specimens of luminescent photographic materials for single and repeated use have been produced. The possibility, in principle, of employing them for recording a phono-

gram over the entire width of the cinefilm, which significantly increases the quality of the sound and leads to the possibility of recording it in a cinecamera, has been demonstrated (M.V.Alfimov).

A method has been developed for the formation of a half-tone image in which the light sensitive component consists of microparticles with immobilised modified enzymes—proteases or enzymes of any class, including oxidases which "work" with a large number of coloured substrates. A model system permitting detection of light fluxes of very low intensity is being studied (I.V.Berezin).

In order to devise non-silver emulsions for the recording of information, studies are being prosecuted on the photochemical reactions in polymer systems incorporating charge-transfer complexes (CTC). Compared with the emulsions already available, the new non-silver emulsions based on charge transfer complexes exhibit a higher light sensitivity, the storage period of the light sensitive emulsion is longer, there is an unusually large photographic latitude, and there is a possibility of obtaining relief and multicolour images (A.V.Vannikov).

Research into the photochemistry of heterocyclic aromatic polyfluoro-compounds is being developed; their interaction with polymeric materials has been investigated and a new light-sensitive composition—the negative FSN-4 photoresistor—has been created on this basis. This made it possible to achieve a photolithographic projection process for the preparation of standard phototemplates for ultrahigh frequency transistors and new semiconductor devices whose operation is based on surface sound waves (V.I.Fokin).

The application of photochemical methods proved effective in the chemistry and technology of polymers. Monolithic organic glasses of any thickness were obtained for the first time on an industrial scale by the photopolymerisation method (S.R.Rafikov and G.P.Gladyshev).

A procedure has been developed for the photochemical modification of polyolefins whereby one can obtain strengthened thermocontracting polyethylene film for the preparation of two-layer thermocontracting insulating tape to be used in the protection of major gas and petroleum pipelines from corrosion.

An important branch of photochemistry is preparative organic photochemistry. The photoinduced *C*-addition of alcohols, acetals, ethers, and esters to acetylene and monosubstituted acetylenes has been investigated. Various olefinic systems with functional group substituents have been obtained with the aid of this reaction (V.F.Kucherov).

The photochemical cycloaddition of α,β-enones to acetylenic substrates and the photorearrangements of the cyclic adducts have been investigated (E.P.Serebryakov).

Methods have been developed for the photochemical synthesis of highly active transition metal complexes to be used in the photoselective metallation of dielectric materials, the liquid-phase oxidation of hydrocarbons, and the accumulation of solar energy. The photochemical reactions of many complexes have been studied (G.A.Shagisultanova).

Laser chemistry. The construction of lasers led to the appearance of a new field of chemistry—laser chemistry. The high intensity and monochromatic nature of the laser radiation makes it possible to exert a powerful selective action on matter. One of the principal advances in this field has been the discovery of the phenomenon of the non-thermal stimulation of chemical reactions by infrared laser radiation (M.G.Basov, E.P.Markin, A.N.Oraevskii, and A.V.Pankratov).

The mechanism of the multiphoton dissociation of 1,2-chlorofluoroethane under the influence of pulsed infrared radiation has been investigated and it has been established that all the decomposing molecules acquire the same energy above the dissociation barrier (~15 kcal mol^{-1}) regardless of the vibrational mode involved in the accumulated energy. The form of the energy distribution function of the decomposing molecules, which satisfies the Boltzmann distribution with an infinitely high temperature and which is "cut off" on the high-energy side (75–78 kcal mol^{-1}), was obtained for the first time (V.N.Panfilov and A.G.Petrov).

A new field of study involving chemical lasers has been established on the basis of the use of chemical chain reactions (G.V.Vasil'ev, V.L.Tal'roze, A.N.Oraevskii, and E.P.Markin).

It has been shown that, in pulse-type chemical lasers based on a mixture of molecular hydrogen and fluorine, it is possible to obtain the energy of coherent emission on initiation of a chain reaction by an electron beam, which exceeds by a factor of 10 the energy of the electron beam consumed in the initiation of the reaction (A.S.Bashkin, A.N.Oraevskii, V.N.Tomashov, and N.M.Yuryshev).

The specific energy utilisation and the efficiency of pulse-type chemical lasers absed on H_2–F_2 and F_2–D_2–CO_2 mixtures have been improved. A new type of continuous action chemical laser, based on the transmission of vibrational excitation from the OH and OD radicals to the CO_2 molecule, has been proposed and constructed. This laser has a specific energy utilisation not inferior to that of the continuous operation laser based on the DF–CO_2 mixture and in addition its "exhaust" products are non-toxic (A.S.Bashkin, A.N.Oraevskii, Yu.P.Neshchimenko, and N.N.Yuryshev).

Laser radiation generation based on the fine structure atomic transitions of iodine and bromine has been achieved; excited iodine and bromine atoms are obtained in the course of chemical pumping. The possibility of the generation of radiation as a result of a branching process in the carbon disulphide oxidation reaction has been demonstrated experimentally (E.B.Gordon).

Laser methods for the separation of isotopes, based on the multiphoton dissociation of molecules under the influence of powerful laser infrared emission, have been developed (V.S.Letokhov and R.V.Ambartsumyan).

Pulse-type and pulse-frequency lasers with an operating range of 11.5–13 μm have been constructed. Successful experiments have been carried out with the aid of these lasers on the separation of carbon isotopes. A pilot plant for the separation of carbon isotopes based on the method of the multiphoton dissociation of CF_3I molecules under the influence of infrared laser radiation is being constructed. The efficiency of the multiphoton dissociation when compound vibrations of the UF_6 and CCl_4 molecules are acted upon has been demonstrated; this makes it possible to employ the existing lasers for isotope separation, which makes the problem of the construction of lasers at a wavelength of 16 μm for the separation of uranium isotopes less acute (E.P.Velikhov, V.S.Letokhov, and A.Z.Grasyuk).

A new field of study, associated with the regulation of a thermochemical process by means of laser radiation, has been established. The principal problem, solved at the present time within the framework of laser thermochemistry, is to control a heterogeneous process on a surface, leading to the formation of film coatings for devices used in microelectronics and laser technology (F.V.Bunkin, B.S.Luk'yanchuk, and A.N.Oraevskii, A.M.Bonch-Bruevich, and Yu.M.Molin).

9. Electrochemistry

Electrochemistry was established as an independent branch of physical chemistry already in prerevolutionary times. Important studies on the nature of the processes at the

metal–electrolyte interface, corrosion, and the passivity of metals have been carried out by I.A.Kablukov, L.V.Pisarzhevskii, D.P.Konovalov, V.A.Kistykovskii, N.A.Izgaryshev, V.A.Plotnikov, and P.P.Fedot'ev.

The expansion of Soviety industry in the first years of Soviet rule led to the development of numerous electrochemical industries—the preparation of aluminium, magnesium, and other non-ferrous metals, the creation of the industry of current sources, etc. This constituted an objective precondition for the intense and fruitful development of electrochemical research in the postrevolutionary period. Fundamental studies were carried out in the newly created institutes and laboratories during the 1930's–1940's, which made it possible to proceed to detailed investigations of the mechanisms of electrochemical processes.

Soviet electrochemical schools now occupy a leading place in world science.

Modern electrochemistry is concerned with the development of the theoretical principles of the transformation of chemical energy into electrical energy, the protection of metals from corrosion, the electrodeposition of metals, the synthesis of various inorganic and organic substances, etc. The Institute of Electrochemistry and the Karpov Institute of Physical Chemistry of the USSR Academy of Sciences, the Institute of Electrochemistry of the Urals Scientific Centre of the USSR Academy of Sciences, the Institute of Physical and Organic Chemistry of the USSR Academy of Sciences in Kazan, the Institutes of the Academies of Sciences of the Ukrainian SSR, the Georgian SSR, the Latvian SSR, the Kazakh SSR, and the Lithuanian SSR, as well as the laboratories of many other institutes and higher educational establishments are working on the solution of these problems.

An outstanding achievement of Soviet Science has been the creation by A.N.Frumkin of the kinetic theory of electrochemical reactions, which has been comprehensively confirmed experimentally and developed further in the studies of his school. The fundamental postulates of the theory include ideas concerning the structure of the electrical double layer, the relation between the rate of an electrochemical reaction and the concentrations of the reactants, the potential jump in the dense part of the double layer on the electron surface, and the influence of the specific absorption of ions and molecules on the electrode process.

The concept of the zero-charge potential has been introduced as an individual characteristic of the metal, which made it possible to solve one of the principal problems of the theory of galvanic cells, namely to find the relation between the electromotive force and the contact potential difference between two metals *in vacuo*.

Novel methods for the investigation of the electrode/electrolyte interface have been devised, namely methods involving the measurements of the capacitance of the electrical double layer by means of an alternating current, the recording of the charging curves, the measurement of the isoelectronic potential shift, etc. Varied information about the structure of this interface on different electrodes and about the influence of various factors on it has been obtained with the aid of these methods (B.V.Ershler, A.I.Shlygin, B.B.Damaskin, O.A.Petrii, V.E.Past, U.Palm, and D.I.Leikis).

Advances have been made in the quantum-mechanical treatment of the elementary charge transfer step in an electrode reaction. A general criterion of the quantum (subbarrier) or classical behaviour of species in the course of homogeneous and heterogeneous reactions in solution has been obtained on the basis of the quantum-mechanical theory. It has been shown that proton transfer takes place mainly via the tunnel mechanism (A.A.Ovchinnikov, G.G.Dogonadze, and A.M.Kuznetsov).

The mechanism of the electrochemical generation of solvated electrons has been studied. The nature of the excited states of solvated electrons and of their associated species has been determined with the aid of laser photolysis in a number of systems. A theory permitting the derivation of quantitative relations between the optical, energetic, and kinetic characteristics of solvated electrons has been developed. The shift of the vibration frequencies of the solvent molecules under the influence of the solvated electron has been observed for the first time by non-linear polarisation Raman spectroscopy. In the interaction of a solvated electron and a hydroxy-radical, obtained by pulse radiolysis, with metal ions, investigators detected metal ions in unusual and unstable oxidation states and studied their physical properties and chemical reactions (A.M.Brodskii, A.V.Vannikov, L.I.Krishtalik, and A.K.Pikaev).

Much attention has been devoted to the study of the kinetics of electrochemical reactions, in particular multistage reactions with electrochemical and chemical stages and reactions involving complex-forming agents. The determination of the kinetic parameters and mechanisms of reactions used in practice made it possible to increase greatly their efficiency (P.I.Dolin, V.V.Losev, L.I.Krishtalik, and V.I.Kravtsov). The appreciable influence of the absorption of ions and organic surfactants on the reaction kinetics and the nature of the products formed has been demonstrated (Ya.M.Kolotyrkin, Z.A.Iofa, and M.A.Loshkarev). The polarographic research method has been significantly developed and the maxima on the polarographic curves and their singularities for irreversible reactions have been explained. New varieties of the polarographic method have been devised. The theory of catalytic hydrogen evolution waves has been developed (T.A.Kryukova, A.G.Stromberg, S.G.Mairanovskii, Kh.S.Brainina, Ya.I.Tur'yan, and Yu.S.Lyalikov).

The studies on electrocatalysis, begun approximately 20 years ago, constitute a logical continuation of the research into electrochemical kinetics. The influence of structural and chemical factors on the activities of various catalysts used in electrochemical reactions, the adsorption and chemisorption of the components and the reactions of intermediates, and the influence of adsorption on the kinetic and catalytic characteristics have been investigated in detail. Active and stable catalysts have been developed for various electrochemical reactions, including the catalysts used in apparatus controlling the composition of the environment (M.I.Temkin, V.S.Bagotskii, V.E.Kazarinov, M.R.Tarasevich, A.G.Pshenichnikov, B.I.Podlovchenko, and Yu.B.Vasil'ev).

A detailed study has been made of the formation of oxide layers on the surfaces of metals and of the mechanism of the passivation of metals. It has been shown that in many cases the passivation is caused by chemisorbed oxygen and not oxides constituting separate phases (Ya.M.Kolotyrkin, B.V.Ershler, I.V.Krotov, B.N.Kabanov, and V.I.Veselovskii).

The Soviet Union occupies a leading position in world science in the field of the physical chemistry of ionic melts and solid electrolytes. The kinetics of electrochemical processes in fused salts and of electrocrystallisation from fused salts have been studied and the structure of the electrical double layer at the fused metal/electrolyte interface has been determined (S.V.Karpachev, O.A.Esin, Yu.K.Delimarskii, A.V.Gorodyskii, A.N.Baraboshkin, S.F.Pal'guev, and E.A.Ukshe).

Studies on the physicochemical properties of both aqueous and non-aqueous electrolyte solutions, which constitute a continuation of those begun at the beginning of this century, have been important for the expansion of the limits of electrochemistry. The fundamental characteristics of the

electrical conductivities of non-aqueous solutions and their relation with solvation and complex formation phenomena have been established. The electrode potentials in various solvents and the characteristic features of many electrochemical reactions in the latter have been determined (N.A.Izmailov, V.A.Pleskov, M.I.Usanovich, O.Ya.Samoilov, G.A.Krestov, Ya.A.Fialkov, and Yu.M.Kessler).

A general theory of ion exchange, on the basis of which hypotheses have been developed concerning the mechanism and the generation of the potential in ion-selective membranes, has been created. New types of glass electrodes and ion-selective electrodes, which are widely used in various branches of the national economy, have been developed (B.P.Nikol'skii and M.M.Shul'ts).

Electochemical institutes, in collaboration with other scientific establishments, have been working on urgent problems in biology and medicine. During the last decade, studies in the field of bioelectrochemistry have been developed. The role of proteins as molecular generators of electrical potentials has been established (Yu.A.Ovchinnikov and P.G.Kostyuk). New electrochemical methods permitting the modelling of membrane enzyme systems capable of transforming energy have been devised (V.P.Skulachev and M.A.Ostrovskii). Laboratory apparatus whereby combined studies can be made on the electrical properties and structures of membranes has been constructed. The electrical stability of membranes has been studied in detail and a theory of this phenomenon has been developed. The cycle of investigations of the induced ion transport through biological membranes and their models has been completed (Yu.A.Chizmadzhev and V.S.Markin). Fig. 16 illustrates the apparatus for the investigation of the membrane coalescence process. It permits visual and electrical monitoring of the process and the separate perfusion of all the solutions in contact with the membranes. Applied investigations, particularly on the electrostimulated coalescence of the lipid vesicles and cells, have begun on the basis of the fundamental research into bioelectrochemistry.

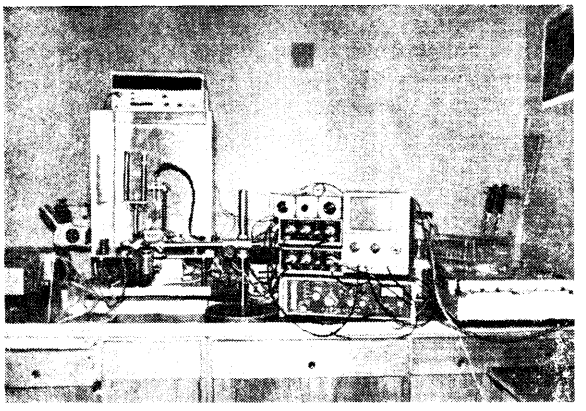


Figure 16. Apparatus for the coalescence of membranes. On the left—experimental cell with microscope; on the right—control and recording apparatus (Institute of Electrical Studies on Chemical Processes of the USSR Academy of Sciences).

A fundamental new technology of the extraction and refining of metals, the formation of alloys, the treatment of metallic surfaces, the formation of single crystals, etc. has been developed and introduced into industry. Considerable progress has been achieved in the synthesis of solid electrolytes and their practical application. A new metallurgical field has been established—the pyroelectrometallurgy of heavy metals in ionic melts. Fundamentally new cathodic and cathodic-anodic refining methods made it possible to obtain the metal with the required purity at a low cost and with a high degree of extraction of products. Theoretical foundations have been created for the application of organic surfactants as factors regulating electrode processes in ionic melts and a technology of the formation of electrodeposited coatings has been developed (Yu.V.Baimakov, N.P.Fedot'ev, A.L.Rotinyan, R.I.Agladze, P.F.Antipin, F.A.Alabyshev, V.P.Mashovets, and V.L.Kheifets).

A general theory of electrocrystallisation has been created in the field of the electrodeposition of metals, a mechanism has been proposed for the levelling and smoothing action of surfactants, and the fundamentals of the theory of the joint discharge of ions with formation of alloys have been formulated. Important data have been obtained on the substructure, phase structure, and physicomechanical properties of electrodeposited layers. Extensive incorporation of galvanic processes in the national economy has been achieved. A chemical-catalytic method of the deposition of metals on a dielectric substance has been investigated and has found extensive applications (J.Matulis, R.M.Vishamirskis, B.A.Purin, K.M.Gorbunova, N.T.Kudryavtsev, V.I.Lainer, G.S.Vozdvizhenskii, Yu.M.Polukarov, and M.V.Gudin).

The undertaking of a series of theoretical and experimental studies was stimulated by the necessity for the development of fuel cells in which chemical energy is directly converted into electrical energy; this involved the investigation of the mechanism of the ionisation of hydrogen and the electrochemical reduction of oxygen, the phenomenon of electrocatalysis, and mass exchange in porous electrodes. The experience gained in research on the hydrogen–oxygen fuel cell has been used to find a method of reducing the potential in the electrolysis of water. Considerable advances have been made also in the development of different versions of chemical current sources (N.S.Lidorenko, O.K.Davtyan, V.S.Bagotskii, R.Kh.Burshtein, N.V.Korovin, and L.N.Dzhaparidze).

A quantitative theory of mass- and heat-transfer phenomena in electrochemical systems, particular in systems with concentrated solutions and intense mass exchange, has been developed (V.S.Krylov and Yu.A.Popov). A theory of the generation and propagation of concentration waves in electrode layers of moving electrolyte solutions has been created and has found technical application in electrochemical information processors. The electrochemical seismic detector and the electrochemical hydrophane make it possible to measure respectively the shifts of the ground and the sonic pressure in an aqueous medium in the range of subsonic frequencies below 10 Hz. The application of electrochemical information processors is promising in seismometry and engineering seismology (P.D.Lukovtsov, B.M.Grafov, and R.Sh.Nigmatullin).

Powerful chlorine electrolysers (mercury and diaphragm), whose principal parameters are up to world standards, have been constructed. A Soviet version of metal oxide anodes has been introduced and is being widely employed. The membrane electrolytic process is being developed and is close to being applied in industry. A highly efficient technology of the manufacture of a number of oxidants—chlorates, perchlorates, persulphates, etc.—has been introduced. New versions of efficient electrolysers for the manufacture of hydrogen are being developed (V.V.Stender, A.L.Rotinyan, L.M.Yakimenko, V.I.Veselovskii, L.I.Krishtalik, and V.V.Losev).

A digital potentiodynamic analyser of water quality of type AKVTs-PD-02, based on the electrocatalytic principle and designed for the rapid determinations of organic impurities in natural, drinking, waste, and environmental water has been constructed (Fig.17). With the aid of this apparatus it is not only possible to determine the overall amount of organic impurities (0.1–1000 mg litre^{-1}) but also to differentiate between them in terms of their oxidisability (V.E.Kazarinov, Yu.B.Vasil'ev, and O.A.Khazova).

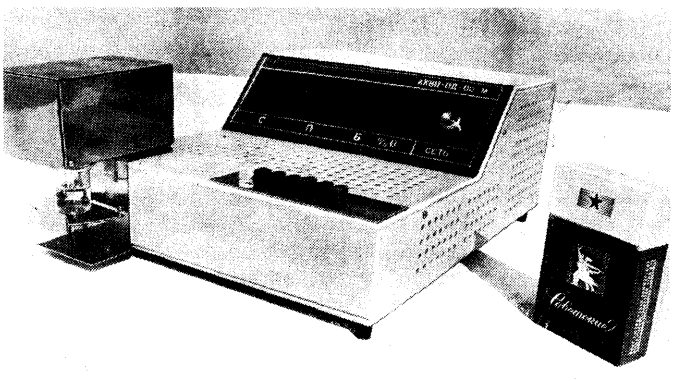


Figure 17. Digital potentiodynamic AKVTs-PD-02 analyser of the quality of water (Institute of Electrochemistry of the USSR Academy of Sciences, Moscow).

Considerable advances have been made in the development of processes for the electrochemical synthesis of organic substances. The adsorption phenomena and the mechanisms of reactions involving organic substances at high anodic potentials have been studied in detail. The industrial manufacture of sebacic acid has been organised on the basis of these investigations. Cathodic hydrodimerisation and anodic halogenation processes involving organic compounds have been optimised. The manufacture of a number of intermediates for the pharmaceutical industry has been initiated (I.L.Knunyants, A.P.Tomilov, M.Ya.Fioshin, V.A.Smirnov, V.E.Kazarinov, G.N.Freidlin, J.Stradins, Yu.P.Kitaev, Yu.M.Tyurin, L.A.Mirkind, D.A.Tedoradze, and L.G.Feoktistov).

Studies on corrosion processes and on the fight aginst corrosion have been widely developed. A theory of multicomponent systems containing metals/solution microsystems of different structure and composition and a theory of coupled reactions have been created. The role of complex formation has been discovered and the direct involvement of water molecules in the electrochemical stages of the dissolution of active metals has been demonstrated experimentally for the first time. It has been shown that a purely chemical mechanism of the dissolution of metals can operate together with the electrochemical mechanism.

Important results have been achieved in the theory of the preparation of corrosion inhibitors. Fundamental research has been carried out on the corrosion mechanism whereby it is possible to develop effective inhibitors of the type of IFKhAN and IFkhANGAZ for the protection of equipment used in the petroleum and gas industries and in the new technology (V.I.Spitsyn). The important role of the electrophysical properties of protecting films has been demonstrated. The principles of the preparation of inhibitors, capable of simultaneously preventing the hydrogen sulphide corrosion, hydrogen embrittlement, and the foaming of adsorbents in sulphur purification processes, have been formulated. New inhibitors protecting steel from cavitation breakdown have been developed and the inhibitors proposed have been introduced in industry.

A new principle of the formation of corrosion-resistant alloys by cathodic doping has been put forward. New steels and alloys resistant to corrosion in corrosive media produced in chemical manufacturing processes, under marine conditions, and in a subtropical atmosphere have been devised. The possibility of predicting the rate of atmospheric corrosion by the method of accelerated tests and from meteorological data has been demonstrated (Ya.M.Kolotyrkin, G.V.Akimov, R.S.Ambartsumyan, N.D.Tomashov, I.L.Rozenfel'd, V.V.Skorcheletti, L.N.Antropov, V.P.Batrakov, Yu.N.Mikhailovskii, and I.K.Marshakov).

10. Chemical Thermodynamics

The most important branches of modern chemical thermodynamics are chemical equilibria, thermochemistry, solutions, physicochemical analysis, and thermodynamics of surface phenomena. The development of chemical thermodynamics in the USSR has a scientific basis laid down by the researches of the Russian scientists G.I.Gess, D.I.Mendeleev, V.F.Luginin, I.A.Kablukov, N.S.Kurnakov, A.V.Rakovskii, and N.N.Beketov. At the present time studies in chemical thermodynamics are stimulated by the necessity to solve important problems such as those arising in the investigation of combustion processes, the creation of new types of fuel, the development of the manufacture of new materials (semiconductors, specially hard, heat resistant, and other alloys, and specially pure substances) as well as problems in the study of the thermodynamic properties and equilibria in various multicomponent systems in relation to separation and purification processes.

Extensive studies on these lines are being prosecuted at the Department of Physical Chemistry of the Faculty of Chemistry of Moscow State University, at the High Temperature Institute of the USSR Academy of Sciences, at the Institute of Chemical Physics of the USSR Academy of Sciences, at the Institute of Metallurgy of the USSR Academy of Sciences, at the Kurnakov Institute of General and Inorganic Chemistry, at the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, at the Mendeleev Moscow Institute of Chemical Engineering, and in other institutes. Modern statistical thermodynamic methods for the calculation of thermodynamic properties are used in connection with this research.

Theoretical studies occupy an important place. A general theory of thermodynamic potentials has been developed on the basis of statistical mechanism. The fundamental thermodynamic concepts have been refined, thermodynamic theory has been formulated more rigorously, irreversible processes have been investigated, and the Second Law of Thermodynamics has been analysed (G.A.Afanas'eva-Erenfest and K.A.Putilov) and geometrical thermodynamics has been developed (A.B.Mlodzievskii). Problems of the thermodynamics of surface phenomena have been dealt with both theoretically and experimentally in the USSR by V.K.Semenchenko and A.I.Rusanov.

The solution–vapour equilibria in complex multicomponent systems have been studied (A.V.Storonkin) and the science of heterogeneous equilibria in multiphase and multicomponent open systems has been developed in relation to geological processes (D.I.Korzhinskii).

Research on the systematic arrangement of data on the thermodynamic properties of substances has been carried on in the Soviet Union for many years and the handbooks "Thermodynamic Properties of Pure Substances" and "Thermal Constants of Substances" have been published (V.P.Glushko, L.V.Gurvich, and V.A.Medvedev). The creation of an automated data bank for thermodynamic properties over a wide temperature range (100–20 000 K) is being completed at the High Temperature Institute of the USSR Academy of Sciences.

M.Kh.Karapet'yants developed a new field of study, which is concerned with the development and application of the methods of comparative calculation of the physicochemical properties of various substances which he proposed; these methods make it possible to calculate a large number of physical and physicochemical constants when a limited number of experimental data are available.

Thermochemical investigations have been based on systematic precision measurements (M.M.Popov and S.M.Skuratov). A series of rules for the determination of the heats of combustion of organic compounds, the heats of formation of inorganic compounds, and the heats and entropies of formation of crystalline substances have been formulated on the basis of experimental thermochemical data (D.P.Konovalov, A.F.Kapushinskii, A.M.Berkengeim, and V.A.Kireev).

The work of Ya.I.Gerasimov and his coworkers has been devoted to an important branch of experimental thermodynamics—the study of heat-resistant alloys, metal oxides, and semiconducting materials. A series of new methods for the determination of thermodynamic quantities at high temperatures have been developed and applied successfully.

Many years of research into the enthalpies of combustion and formation of arene, cyclopentadiene, carbonyl, and mixed compounds of transition metals have been completed (I.B.Rabinovich).

The new phenomenon of the limited miscibility of gaseous phases has been investigated and observed for a number of systems and a study has been made of the solubility of gases in liquids at elevated pressures (I.R.Krichevskii).

Theoretical and experimental studies on mass exchange at high flow rates are being carried on in order to develop highly intensive mixture separation processes. An automated experimental system for the determination of mass transfer coefficients in gaseous and liquid phases, incorporating the determination of the humidity of the gas and the presence of the gas in the liquid has been devised (N.M.Zhavoronkov and V.A.Malyusov).

The problem of chemical equilibria in complex mixtures at high temperatures is important for many branches of engineering. The equilibria in the thermal and catalytic cracking of hydrocarbons have been studied experimentally (A.V.Frost and A.A.Vvedenskii) and methods have been developed for thermodynamic calculations on processes in combustion and explosion (Ya.B.Zel'dovich and Yu.M.Shaulov). Systematic calculations of thermodynamic quantities for gases at high temperatures are related to the same field (I.N.Godnev, L.V.Gurvich, and K.S.Krasnov).

The thermodynamic functions for individual inorganic compounds, groups of compounds, solutions, and alloys have been studied by many investigators in connection with practical problems and theoretical generalisations. Mention may be made of the work of A.F.Kapustinskii, E.V.Britske, V.A.Sokolov, N.K.Voskresenskii, A.I.Vol'skii, A.A.Zhukhovitskii, V.A.Kireev, G.V.Kurdyumov, K.P.Mishchenko, M.M.Popov, K.G.Khomyakov, A.N.Nesmeyanov, A.M.Samarin, N.V.Ageev, I.I.Kornilov, and S.A.Shchukarev.

The thermodynamics of aqueous and non-aqueous solutions has been developing successfully (G.A.Krestov and A.F.Vorob'ev). The work of V.M.Eremenko, G.M.Lukashenko, A.G.Morachevskii, and L.F.Kozin has made a large contribution to the thermodynamics of alloys. The studies by N.A.Vatolin have been devoted to the thermodynamics of metallurgical processes.

A large series of studies have been performed in recent years on the chemical thermodynamics of semiconductors in order to establish the scientific foundations of the controlled synthesis of semiconducting materials: new relations between thermodynamic quantities have been derived, new experimental methods for the determination of the thermodynamic characteristics of substances have been devised, and ways have been developed for their estimation and calculation (A.V.Novoselova, Ya.I.Gerasimov, G.F.Voronin, V.M.Glazov, A.S.Pashinkin, F.A.Kuznetsov, B.A.Popovkin, V.P.Zlomanov, V.B.Lazarev, A.R.Regel', and Ya.A.Ugai).

11. The Liquid State of Matter

Pure liquids and liquid solutions have been investigated in the USSR. The classical studies by D.K.Chernov, D.P.Konovalov, V.F.Alekseev, I.M.Sechenov, I.A.Kablukov, V.A.Plotnikov, P.I.Val'den, A.N.Sakhanov, B.V.Golitsyn, and P.F.Shreder are widely known. Research into the liquid state of matter is being actively prosecuted on many different lines, being closely intertwined with other fields of study.

The methods of physicochemical analysis, devised by N.S.Kurnakov, S.F.Zhemchuzhnyi, N.I.Stepanov, and V.Ya.Anosov and developed further in the studies of A.V.Novoselova, Ya.I.Gerasimov, I.V.Tananaev, G.G.Urazov, A.A.Bergman, and many other investigators are being widely applied. The laws of D.P.Konovalov and M.S.Vrevskii serve as a basis of theory and practice in distillation and fractionation processes. In the course of precision investigations, the limited miscibility of gases, ternary critical points, a series of unexpected properties of critical infinitely dilute solutions—gas systems, and the cessation of diffusion at the consolute point have been discovered (I.R.Krichevskii, P.E.Bol'shakov, D.S.Tsiklis, G.D.Efremova, and N.E.Khazanova). An equation has been proposed for the solubility of gases in liquid at high pressures and its solution has been found (I.R.Krichevskii, I.A.Kazarnovskii, and I.L.Leites).

Fundamental studies on the thermodynamic and other properties of liquid dielectrics and electronic and ionic melts have been carried out by V.A.Kirillin, A.E.Sheindlin, Yu.K.Delimarskii, M.P.Vukalovich, I.I.Novikov, Ya.I.Gerasimov, A.R.Regel', K.P.Gurov, G.A.Krestov, L.R.Fokin, A.K.Abas-Zade, Kh.I.Amirkhanov, A.M.Karimov, and V.M.Glazov. Studies have been made on the preparation of ultrapure liquids (G.G.Devyatykh and V.A.Mikhailov). The influence of isotopic substitution on the physicochemical properties of liquids has been investigated (I.B.Rabinovich). L.P.Filippov studied systematically the thermal conductivities of liquids and proposed more than 40 methods for the calculation of the properties of liquid substances of practical importance with the aid of the theory of corresponding states.

Theoretical and experimental studies have been carried out on heterogeneous equilibria involving liquid phases (A.V.Storonkin, A.I.Rusanov, A.G.Morachevskii, N.P.Markuzin, M.M.Shul'ts, N.A.Smirnova, and V.B.Kogan).

The determination of the relation between the properties of liquid systems and their structure and the elucidation of the molecular mechanisms of the processes occurring spontaneously in the course of the thermal movements of liquids or arising in liquid systems under the influence of external stimuli are the fundamental problems of the theory of liquids.

The work of Ya.I.Frenkel', summarised in his familiar monograph "The Kinetic Theory of Liquids", has been of great importance in the solution of this problem. Frenkel' examined the problem of the order in the positions of neighbouring molecules of liquids resembling the order in crystals. The theory of the thermal movement of the molecules of liquids with the aid of the concept of the Brownian migration of solid particles has been developed (K.A.Valiev and E.N.Ivanov).

Another approach, based on the methods of statistical mechanics, was developed by N.S.Bogolyubov. Starting from a simple model of a gas or liquid consisting of spherical particles interacting via central additive forces, Bogolyubov derived equations for the correlation functions determining the inter-relations between the species. This permitted the development of the molecular theory of the properties of simple systems similar to liquid argon and to obtain Debye formulae in the theory of strong electrolytes. A series of versions of the statistical theory of liquid systems, based on the above model, have been proposed in the studies of I.Z.Fisher, A.A.Vlasov, A.E.Glauberman, S.V.Tyablikov, L.A.Rott, I.R.Yukhnovskii, A.A.Adkhamov, G.A.Martynov, Yu.P.Syrnikov, Yu.M.Kessler, and R.M.Yul'met'ev. Some problems of the statistical mechanism of liquids have been considered by A.M.Evseev with the aid of the methods of molecular dynamics.

A relation has been established between fluctuations, second-order phase transitions, and critical phenomena (V.K.Semenchenko). A.Z.Pokrovskii, V.L.Patashinskii, and M.A.Anisimov made a considerable contribution during the 1970's to the development of this problem with the aid of the method of similarity.

Fundamental studies on surface tension and boundary layers in non-electrolyte and electrolyte solutions have been carried out by P.A.Rebinder, B.V.Deryagin, E.D.Shchukin, N.V.Churaev, A.I.Rusanov, and G.I.Fuks. A series of precision measurements of the surface tensions of liquid metals and alloys have been performed (V.K.Semenchenko, S.N.Zadumin, P.P.Pugachevich, N.L.Pokrovskii, and Kh.I.Ibragimov).

The discovery of new experimental methods has promoted the development of research into the liquid state of matter. L.I.Mandel'shtein predicted theoretically and E.F.Gross observed for the first time the fine structure of the isotropic scattering of light in liquids. The fine structure of the anisotropic light scattering has been discovered (I.L.Fabelinskii). These investigations made it possible to devise optical methods for the study of ultrafast processes in liquids.

Various optical methods for the investigation of matter have been devised and a major contribution has been made to the molecular theory of liquid systems. The EPR method has been used to study liquids. Solutions have been investigated by the method of dielectric microwave spectroscopy (O.A.Osipov).

L.F.Vereshchagin devised a method for the creation of high and ultrahigh pressures, which made it possible to obtain valuable information about the properties of liquids at high pressures.

The first studies of the structure of liquids with the aid of X-ray scattering in our country are due to V.I.Danilov. They were continued by I.V.Radchenko and A.F.Skryshevskii.

Fundamental researches have been made into the viscosities of all the main types of liquid systems (A.I.Bachinskii, A.Z.Golik, E.G.Shvidkovskii, N.P.Rudenko, G.M.Panchenkov, and V.M.Glazov).

New acoustic methods have been devised and experimental and theoretical studies have been made on the acoustic properties of pure liquids and liquid solutions (I.G.Mikhailov, V.A.Solov'ev, B.B.Kudyavtsev, V.I.Ilgunas, V.F.Nozdrev, A.N.Berdyev, P.K.Khabibullaev, and N.B.Leshnev). Sonochemical processes in solutions have been discovered and are being successfully investigated (M.A.Margulis).

M.I.Shakhparonov carried out numerous optical, thermodynamic, radiophysical, and acoustic studies on liquid systems. He created new methods for the investigation of the interaction of molecules and the mechanisms of slow, rapid, and ultrarapid non-collective and collective processes occurring during the thermal movement of liquid substances (Fig.18). A molecular theory which elucidates the significance of many phenomenological coefficients of non-equilibrium thermodynamics has been developed. A contribution has been made to the theory of fluctuations in solutions. The existence of second-order phase transitions in liquid systems has been established. The molecular mechanis of the action of depressor additives to motor fuels and oils has been examined (A.P.Grishin).

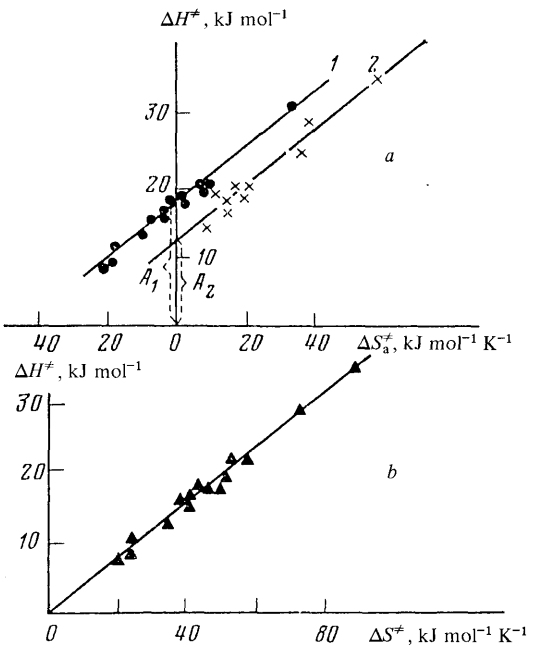


Figure 18. Isokinetic effect in the H-bond dissociation (line *1*) and H-bond transfer (line *2*) reactions in alcohols ROH: a) the apparent activation entropies $\Delta S_a^{\neq}$ for the corresponding reactions are plotted along the abscissa; *b*) the true entropies of activation $\Delta S^{\neq}$ for the same reactions are plotted along the abscissa.

Studies in the field of aqueous and non-aqueous electrolyte solutions have been carried out by L.A.Pisarzhevskii, A.I.Brodskii, and V.A.Pleskov. Important research in the field of the theory of acids and bases has been carried out by A.I.Shtenshtein and M.A.Usanovich.

The concept of ion pairs in electrolyte solutions was introduced for the first time and the theory of such pairs was proposed (V.K.Semenchenko). A quantitative theory of the thermodynamic properties of electrolyte solutions has been created (N.A.Izmailov). The thermodynamics and structures of aqueous and non-aqueous electrolyte solutions have been investigated (K.P.Mishchenko and G.M.Poltoratskii). The

chemistry of natural waters and methods for their analysis have been investigated by O.A.Alekin.

V.Kireev, A.F.Kapustinskii, K.B.Yatsimirskii, and G.A.Krestov have studied the thermodynamics and kinetics of the processes occurring in electrolyte solutions. Mention should be made of a series of investigations performed by G.I.Mikulin, S.V.Gorbachev, S.I.Drakin, Ya.A.Fialkov, V.A.Mikhailov, A.B.Zdanovskii, Yu.Ya.Fialkov, S.P.Miskidzhyan, Yu.A.Dyadin, I.A.Mirtskhulava, and V.V.Aleksandrov.

B.P.Nikol'skii investigated the mechanisms of oxidation and reduction processes in solutions (oxidation-reduction titrations). The negative hydration of ions has been observed and a number of problems concerning the structure of aqueous solutions have been examined (O.Ya.Samoilov). The kinetics of crystallisation and evaporation processes involving liquid systems have been investigated (V.P.Skripov and E.N.Nesis). Liquid crystals, which are of great practical and theoretical importance, have been vigorously investigated during the last decades (Yu.V.Vul'f, A.B.Mlodzeevskii, A.V.Shubnikov, B.K.Vainshtein, V.N.Tsvetkov, I.G.Chistyakov, A.P.Kapustin, S.A.Pikin, and M.M.Blinov).

Soviet scientists have made a large contribution to the study of quantum liquids.

12. Adsorption and Chromatography

Adsorption phenomena play an important and frequently decisive role in many processes involving the purification, recovery, and separation of substances, in catalysis and corrosion, and in the formation of modified polymer compositions.

The fundamental research by Russian scientists in the prerevolutionary period laid the foundations for the studies of adsorption in the USSR. The extensive experimental and fundamental theoretical investigations by M.S.Tsvet, A.A.Titov, N.A.Shilov, and A.V.Rakovskii have gained world renown.

The work of N.N.Semenov, Yu.B.Khariton, and A.A.Shal'nikov has played a major role in the development of modern molecular-kinetic ideas concerning the theory of adsorption and capillary condensation. These studies and the pioneer investigations of V.V.Il'in, V.V.Tarasov, and V.K.Semenchenko, devoted to the creation of an electrical theory of adsorption, served as a basis for the development of research in our country in the field of the molecular-statistical theory of adsorption and the theory of intermolecular interactions in adsorption systems (A.N.Frumkin, B.V.Deryagin, G.A.Martynov, D.P.Potkus, A.A.Lopatkin, A.V.Kiselev, V.A.Bakaev, M.I.Temkin, A.I.Rusanov, F.M.Kunin, V.I.Shimulis, E.D.Shchukin, A.A.Zhukhovitskii, and V.K.Semenchenko). As a result of these researches, not only have our ideas about the phenomenon of adsorption deepened but also it has become possible to predict the behaviour of adsorption systems.

Problems of hydrodynamics and mass and heat transfer in adsorption, fractionation, and molecular distillation processes have been the subject of studies by N.M.Zhavoronkov.

A set of computer programs have been devised for the investigation of adsorption in all stages of saturation by the method involving numerical experiments (Institute of Physical Chemistry of the USSR Academy of Sciences, Institute of Physical and Organic Chemistry of the Academy of Sciences of the Georgian SSR, and Tbilisi University). Molecular-statistical calculations of the Henry constants for the adsorption of molecules in combination with the experimental values permitted the development of a new structural-chemical method for the study of substances—chromatoscopy (Moscow State University and the Institute of Chemistry and Chemical Technology of the Academy of Sciences of the Lithuanian SSR)

The complexity of the real adsorption systems and the impossibility of carrying out calculations for them on the basis of intermolecular interaction data alone required the development of experimental studies and a thermodynamic approach to their explanation as well as the development of methods for the calculation of the adsorption equilibrium from a minimal amount of empirical information.

Modelling of the elementary steps of the interaction of the liquid and solid phases with the aid of a computer made it possible for the first time to discover the molecular mechanism and the dynamics of wetting and of the spreading of liquids and to trace the involvement of surfactant molecules in these processes (Institute of Chemical Physics of the USSR Academy of Sciences).

The greatest achievements are associated with the work of M.M.Dubinin and his coworkers on the creation of a theory of adsorption applicable to the majority of adsorption systems of practical importance. On the basis of a minimal amount of empirical information, this theory, called "the theory of the volume saturation of micropores", permits the calculation of the adsorption equilibrium over a wide range of temperatures and pressures for vapours of any substances. The adsorption of water vapour on activated charcoals has been investigated in detail for different coverages. An equation for the calculation of the dynamic activity of the layer of activated charcoal with respect to highly volatile substances has been obtained on the basis of the kinetic characteristics of the adsorption process. This permits the determination of the optical dimensions of the micropores for the effective adsorption of highly volatile substances under the conditions of a high moisture saturation of the adsorbents.

The work of A.I.Rusakov, B.P.Bering, V.V.Serpinskii, V.A.Bakaev, V.I.Shimulis, A.A.Lopatkin, A.V.Kiselev, K.V.Chmutov, O.G.Larionov, and A.M.Tolmachev has made a large contribution to the thermodynamic theory of adsorption. It permitted not only the calculation of the thermodynamic characteristics of the behaviour of adsorption systems but also in many cases the prediction of their behaviour was possible.

A theory of the adsorption of individual gases and gaseous mixtures, which has been called the osmotic theory of adsorption, has been developed in recent years by B.P.Bering and V.V.Serpinskii on the basis of the thermodynamics of solutions using the vacancy solution model. The theory yields a rigorous equation of state for the adsorption phase and equations for the adsorption isotherm; it permits the prediction of the behaviour of an adsorption system over a wide range of temperatures and pressures; the adsorption of a mixture of substances can be predicted from the adsorption of the individual components, measured at a single temperature. From the adsorption isotherms the relation between the deformation of sorbents on the amount of sorbed substance can be found.

A thermodynamic method for the prediction of the nature of the sorption of solutions on the basis of the adsorption isotherms of the individual components has been developed as a result of experimental studied of the adsorption of individual vapours and solutions (K.V.Chmutov, O.G.Larionov, A.M.Tolmachev, and A.V.Kiselev). Fundamental studies have been carried out on the heat capacities of adsorption systems whereby the rules governing two-dimensional condensation in the adsorption layer have been discovered (A.V.Kiselev and G.I.Berezin).

The studies by N.A.Shilov and his school of the adsorption of solutes on carbon were the first to demonstrate the presence on carbon of oxides of different chemical types; the ion-exchange nature of the adsorption of electrolytes on

carbon was demonstrated for the first time in the above investigations (M.M.Dubinin, L.K.Lepin', and K.V.Chmutov). These researches laid the foundations of two new fields in the study and applications of adsorption processes—the chemistry of surfaces and ion exchange on synthetic materials. The studies of A.V.Kiselev in the chemistry of surfaces led to the creation of a series of new promising adsorbents with specified properties. This field is being successfully developed by I.E.Neimark, A.A.Chuiko, and V.A.Tertykh. A rapid and informative polarographic method has been proposed for the investigation of the chemistry of the surfaces of charcoals and the adsorption of solutes (V.Yu.Glushchenko). V.I.Gol'danskii and I.E.Neimark used Mössbauer spectroscopy to investigate silica-based adsorbents. The paramagnetic probe method has proved extremely fruitful in the study of adsorption and heterogeneous catalysis (V.B.Golubev, E.V.Lunin, and A.K.Selivanovskii).

The adsorption and catalytic properties of adsorbents and catalysts are in many respects determined by their structure and the size and dimensions of pores. A classification of sorbents in accordance with the porous structure has been proposed on the basis of fundamental researches in this field and differences in the nature of the adsorption on adsorbents of different types have been demonstrated. Studies in this field have been carried on by the schools of M.M.Dubinin, A.V.Kiselev, T.G.Plachenov, G.K.Boreskov, M.I.Temkin, I.E.Neimark, and R.Kh.Minachev. A theory of the corpuscular structure of gel-forming adsorbents has been devised; methods have been proposed on its basis for the specific modification of the porous structure of silica gels (A.V.Kiselev and Yu.S.Nikitin). Methods have been devised for the investigation of gel formation in the secondary porous structures of adsorbents and the structures of various types of charcoals have been investigated (T.G.Plachenov).

The fundamental researches carried out have served as a basis for the development of various types of sorbents and catalysts. New methods for the preparation of mineral adsorbents of practical importance have been devised by A.V.Agafonov and M.A.Kaliko. The manufacture of synthetic zeolites—a most important raw material for the formation of catalysts and one of the most interesting types of adsorbents—has been organised in the USSR as a result of the work of M.M.Dubinin, G.V.Tsitsishvili, S.P.Zhdanov, I.E.Neimark, B.A.Lipkind, Ya.V.Mirskii, L.I.Pigudova, and N.F.Meged'. V.M.Chertov devised a theory of the hydrothermal synthesis of mineral sorbents which made it possible to obtain mineral adsorbents with different porous structures. I.V.Grebenshchikov discovered porous glasses. Subsequent studies by S.P.Zhdanov and D.P.Dobychin made it possible to devise methods for the specific regulation of the structures of these adsorbents. T.G.Plachenov and his coworkers developed ways of obtaining carbonaceous molecular sieves.

In recent years studies in this field have been directed to the preparation of sorbents with specified properties. The characteristics of the synthesis of high-silica zeolites from available initial reactants have been studied at the Institute of the Chemistry of Silicates of the USSR Academy of Sciences and a waste-free highly efficient technology of the preparation of a high-silica zeolite, namely erionite, has been proposed at the Kola Branch of the USSR Academy of Sciences. A new group of catalysts, which permit the selective hydrocracking of petroleum fractions with moderate and high boiling points, expanding thereby the available resources for the preparation of reactive fuels, has been developed on the basis of high-silica zeolites.

At the same time the country's needs for sorbents in the petroleum, chemical, and food industries have been responsible for the large scale of the scientific research into natural highly disperse minerals and their applications as adsorbents and catalysts.

Systematic studies have been carried out on the adsorption properties and structures of natural adsorbents from Far Eastern and Siberian deposits (V.T.Bykov) and the Volga region fuller's earths (N.N.Gryazev, F.M.Rakhovskaya, and F.A.Slisarenko) and methods are being developed for improving the adsorption properties of the clays from the Ukraine (F.D.Ovcharenko, Yu.I.Tarasevich, and N.G.Taran). Studies on the adsorption-structural characteristics of Georgian bentonite clays demonstrated the possibility of using them for the purification and drying of petroleum products and for the chromatographic separation of hydrocarbons (A.A.Tvalchrelidze, G.V.Tsitsishvili, S.S.Filatov, and M.S.Mirabishvili). Bleaching properties have been discovered in a series of clays from Moldavia in relation to petroleum products and plant oils (P.K.Migal' and M.A.Kerdivarenko). Methods for the activation of the clays of Uzbekistan (B.I.Ezdakov, L.B.Smolina, M.D.Ryabova, E.A.Aripov, and K.S.Akhmedov) and Kazakhstan (Sh.B.Battalov) have been devised and standardised. In the Azerbaijan SSR natural sorbents have been widely introduced into the petrochemical industry of the republic as a result of the studies by Z.G.Zul'fugarov and coworkers, who were the first to establish a relation between the chemical composition, the activation conditions, and the physicochemical properties of natural activated clays and their adsorption and bleaching capacities.

Ion exchange, which is one of the forms of chemisorption, plays an important role in nature and has been used for a long time for practical requirements. As early as 1909, N.N.Zimin used ion-exchange filters for the softening of water.

The studies of B.B.Nikol'skii, E.N.Gakov, K.V.Chmutov, P.P.Nazarov, N.N.Mostorina, B.N.Laskorin, M.M.Senyavin, S.Yu.Elovich, V.P.Meleshko, V.A.Pasechnik, G.V.Samsonov, V.I.Paramonova, S.E.Bresler, E.M.Savitskaya, V.P.Bruns, V.I.Gorshkov, A.M.Tolmachev, K.M.Saldadze, Yu.A.Kokotov, N.I.Nikolaev, V.D.Kopylova, and V.S.Soldatov led to the development of theoretical ideas in the field of ion exchange which permitted a wide-scale application of ion-exchange resins in the national economy. The work of I.P.Losev, E.B.Trostyanskaya, A.S.Tevlinov, A.B.Davankov, A.B.Pashkov, B.N.Laskorin, and K.M.Saldadze created the industry of ion-exchange resins and membranes which satisfies the requirements of the national economy for these materials. In recent years the efforts of investigators have been directed to the creation of materials with an enhanced selectivity, improved kinetic properties, and an increased resistance to radiation.

One of the most important applications of adsorption phenomena is their utilisation for the separation of substance, which is usually carried out under dynamic, i.e. chromatographic conditions.

The theoretical principles of chromatographic separation have been developed in the studies of M.M.Dubinin, A.A.Zhukhovitskii, O.M.Todes, K.V.Chmutov, E.N.Gapon, S.Z.Roginskii, and V.V.Rachinskii. Mathematical models of sorption dynamics, whereby separation processes can be simulated, have been set up and a theory of separation in a moving and fluidised bed has been developed. Mathematical modelling of processes involved in the ion-exchange sorption kinetics has been developed by B.N.Laskorin and his coworkers, K.V.Chmutov and A.I.Kalinichev, P.E.Tulupov, G.A.Chikin, and I.O.Bogatyrev. The results of these studies have been used to optimise the separation of cerium and europium, to purify the alkylation reaction mixture in the manufacture of alkylbenzene, and in the preparation of high-fructose alcohols.

A series of new versions of chromatography have been devised. M.S.Shraiber and A.V.Andreev studied thin-layer chromatography. A team of research workers in the Siberian Division of the USSR Academy of Sciences proposed the method of capillary liquid chromatography which has an efficiency not inferior to that of the usual high-efficiency liquid chromatrography and at the same time enables one to economise on materials and to analyse extremely small amounts of substances. A.A.Zhukhovitskii and M.M.Turkel'taub developed the chromathermographic and heat-dynamic methods, the method of chromatography without carrier gas, chromadistillation, and the method involving repeated thermal adsorption concentration whereby the concentration of the impurity in the mixture can be increased by a factor of hundreds with a consequent improvement of the sensitivity and accuracy of the analyses for microimpurities. The method of ligand exchange chromatography is extremely effective in the analysis of stereoisomers (V.A.Davankov).

Gas-chromatographic methods have been developed further (V.G.Berezkin and M.S.Vigderauz).

Novel methods have been created for the synthesis of highly efficient glass capillary columna (E.A.Mistryukov and B.A.Rudenko). The thermodynamic treatment of the polarity and selectivity of gas-chromatographic sorbents has been proposed and gas-chromatographic methods for the identification of the components of odours have been successfully developed (R.V.Golovnya). The studies of V.P.Chizhkov were devoted to problems of the separation of complex mixtures by circulation chromatography; gas extraction methods in chromatographic analysis have been developed in the investigations of B.V.Ioffe; theoretical and experimental studies on the applications of chromatography to the industrial separation of components have been carried out by K.I.Sakodynskii. In his work M.I.Yanovskii investigated and carried out chemical reactions under gas-chromatographic conditions; the research of G.V.Tsitsishvili, T.G.Andronikoshvili, and A.V.Kiselev has been devoted to problems of the utilisation of zeolites in gas chromatography; E.A.Kyullik has been studying the methods of correlation chromatography whereby the sensitivity of the determinations can be increased by a factor of hundreds.

Highly efficient liquid chromatography, which, together with X-ray diffraction analysis, ultracentrifugation, and electron microscopy ensured the greater successes in molecular biology, has been developing at the highest rate in recent years (B.G.Belen'kii, A.N.Vul'fson, and G.G.Vasiyarov). The method has found extensive applications in the analysis of rubber compositions (E.L.Styskin) and the analysis of oligomers and polymers (S.G.Entelis, A.I.Kuzaev, D.D.Novikov, B.G.Belen'kii, and E.S.Gankina). Chromatographic methods are being used to analyse objects in the environment (M.M.Senyavin and G.V.Golovkin), in the analysis and regulation of petrochemical manufacturing processes (V.G.Berezkin and V.N.Lipavskii), in the food industry (K.M.Ol'shanova and N.V.Makarov), and in medicine (Z.A.Zurabashvili); chromatographic methods for the diagnosis of a number of diseases have been devised (R.T.Togozov).

The development of theoretical and experimental studies in sorption and chromatography have stimulated analytical instrument making.

New models of chromatographs of the "Tsvet" and "Biokhrom" types have been mass-produced.

An analytical liquid-type chromatograph for the analysis of natural and synthetic compounds has been designed and constructed.

Highly sensitive laser aerosol spectrometers have been constructed. The development of apparatus for the investigation of the sorption dynamics of multicomponent systems has been completed.

The applications of chromatography are being expanded; it is becoming to an increasing extent the method for the preparative and industrial separation of complex mixtures. Chromatographic methods are used for the industrial isolation and purification of medicinal preparations (G.V.Samsonov, V.A.Pasechnik, and Yu.V.Shostenko), for the separation of lanthanide, transuranic, and alkaline earth metals (K.V.Chmutov and P.P.Nazarov), for the purification and separation of petroleum products (L.S.Kofman, S.Z.Levinson, D.I.Orochko, I.A.Mikhailov, and O.G.Larionov), for the purification of food products (G.A.Chikin), for the purification of waste water and the extraction of non-ferrous metals (G.A.Chikin, V.D.Kopylova, and N.N.Matorina), for the desalination of water (K.M.Saldadze and A.Ya.Shatalov), for the separation of non-ferrous metals (B.N.Laskorin and E.I.Kazantsev), and for the isolation of proteins, enzymes, and oligopeptides (G.V.Samsonov and V.A.Pasechnik).

In this connection there has been a growth of interest in the organisation of highly productive continuous separation processes in fluidised beds (V.I.Gorshkov) and in a rotating column (K.V.Chmutov and A.Ya.Pronin) and in the solution of problems of improving the efficiency of large-diameter columns (K.I.Sakodynskii).

13. Colloid Chemistry

Systematic studies on disperse systems were carried out at the beginning of the XXth century by A.V.Dumanskii—the founder of the first independent colloid-chemical laboratory.

After the Great October Socialist Revolution, large centres working in the field of colloid chemistry were established in the USSR Academy of Sciences, branch institutes, and higher educational establishments. Important research has been performed by N.P.Peskov, I.I.Zhukov, S.M.Lipatov, A.I.Rabinovich, A.N.Frumkin, P.A.Rebinder, D.L.Talmud, and B.V.Deryagin. As a result of these investigations and particularly the work of P.A.Rebinder, modern colloid chemistry was formulated as the science of the unusual properties of matter due to the disperse heterogeneous state, which is of universal importance in nature and in technological processes, and of the decisive role of surface phenomena in disperse systems.

Soviet scientists have assumed a leading role in the establishment of the modern science of the stability of disperse systems. N.N.Peskov formulated ideas concerning the kinetic and aggregative stability of colloids as a function of their degree of dispersion and kinetic and adsorption properties (N.N.Peskov). The molecular attraction forces were measured for the first time and their comparison with the repulsion forces of the diffuse layers of counterions made it possible to set up a rigorous quantitative theory of the stability and electrolytic coagulation of hydrophobic sols (B.V.Deryagin and L.D.Landau).

P.A.Rebinder and his students V.I.Likhtman, G.V.Karpenko, E.D.Shchukin, Yu.V.Goryunov, and M.V.Pertsov determined the molecular mechanisms and conditions of the manifestation of the "Rebinder effect"—the phenomenon of the adsorption facilitation of the decomposition, deformation, dispersion, and mechanical treatment of solids as a consequence of the decrease of the surface energy at the interface between the solid and the surface-active medium; the general character of this phenomenon and its wide-scale occurrence in geological processes have been demonstrated.

Credit for the experimental and theoretical studies on the processes involved in the formation and regulation of the stability of disperse systems as well as new ideas concerning lyophilic colloids as thermodynamically stable disperse systems

formed spontaneously is due to P.A.Rebinder and his school. Direct measurements have been made of the cohesive forces between particles in different media as a function of the lyophilic properties of the system, i.e. the intensity of the interphase interaction; quantitative estimates have been made of the adhesion energy and a thermodynamic theory of the transition from stability to coagulation and the formation of a structure has been developed on this basis (E.D.Shchukin).

The science of surface forces, the structure of boundary liquid layers, and the wedging pressure has been developed by B.V.Deryagin. Ideas concerning various components of the wedging pressure have been used widely in the calculation of the stabilities of films and colloids and in the solution of problems of membrane separation. A new theory of the equilibrium in and the flow of non-freezing layers and films of water in frozen ground has been proposed on their basis (B.V.Deryagin and N.V.Churaev). New data concerning the structure of boundary layers of water in dispersions of a number of silicates have been obtained by NMR and EPR (F.D.Ovcharenko, Yu.I.Tarasevich, and V.V.Mank).

Electrical surface phenomena in finely porous membranes and other disperse systems have been studied in detail by I.I.Zhukov and coworkers. A theory of non-equilibrium electrokinetic phenomena has been developed by S.S.Dukhin; together with B.V.Deryagin, they created a theory of new electrical surface phenomena—diffusiophoresis and capillary osmosis.

Soviet scientists have made a significant contribution to the establishment of the science of the formation of spatial structures—three-dimensional networks of particles in concentrated disperse systems, which determine their mechanical (rheological) properties. P.A.Rebinder was the first to formulate the concept of the qualitative difference between the coagulation contacts between particles in thixotropic suspensions, pastes, powders, on the one hand, and the phase contacts in condensation-crystallisation structures, on the other.

A new large field of modern colloid chemistry—physicochemical mechanics, in which the scientific principles of the procedures ensuring the required structure and the necessary mechanical properties of a wide range of materials are deduced—has been established on the basis of fundamental investigations of structure formation in disperse systems and of the influence of the medium on the cohesive forces between the particles and the strength of solids (P.A.Rebinder); it has served as a basis for the construction of the modern theory of the hardening of mineral binders (E.E.Segalova, A.F.Polak, and V.B.Ratinov), the formulation of the optimum technology of their application in building materials, and the development of the scientific principles of the intensification of technological processes in concentrated disperse systems (N.B.Ur'ev).

The colloid chemistry of disperse minerals has been greatly developed; studies have been made of the ion-exchange properties of clays, zeolites, and soils, and methods and a technology of the preparation of catalysts, sorbents, and fillers for polymeric materials on the basis of natural minerals as well as procedures for controlling the structures of borax wash solutions, ceramic compositions, and different types of soils.

Modern methods and instruments for comprehensive study of the rheological characteristics of structured disperse systems have been devised by M.P.Volarovich, A.A.Trapeznikov, and G.V.Vinogradov.

I.V.Petryanov-Sokolov's studies in the physical chemistry of aerodisperse systems led to the development of quantitative methods for the experimental investigation of the degrees of dispersion of aerosols and to the solution of a number of problems concerning their electrical properties. Important investigations of the conditions in the formation and coagulation of smoke and mists, methods for controlling these processes, and the development of procedures for the monitoring and elimination of suspended particles from gases have been carried out by V.A.Fedoseev, N.A.Fuks, Ya.I.Kogan, A.G.Amelin, B.V.Deryagin, and P.S.Prokhorov.

The methods proposed by B.V.Deryagin and D.V.Fedoseev and based on phase transitions in thin carbon layers constitute a new field in the synthesis of diamond.

In connection with the wide-scale incorporation of surfactants in various branches of the national economy, the physical chemistry and technology of such substances have developed rigorously. The hypothesis of the existence of a series of fundamentally different mechanisms of their action, determined by the structure of the adjoining phases and surfactant molecules as well as the conditions in their adsorption, has been extended (P.A.Rebinder, A.B.Taubman, and E.D.Shchukin). The colloid chemistry of nonaqueous surfactant solutions has developed successfully (G.I.Fuks).

The colloid chemistry of polymers has undergone a comprehensive development. New effective methods for the filling of polymers with disperse minerals and fibres have been devised (N.S.Enikolopov, F.D.Ovcharenko, Yu.S.Lipatov, S.S.Voyutskii, and V.N.Kuleznev); a wide variety of polymeric surfactants, which are effective regulators of the properties of disperse systems, have been synthesised and have found extensive applications (K.S.Akhmedov); metallopolymeric materials and coatings proved to be excellent (E.M.Natanzon, Yu.F.Deinega, and Z.R.Ul'berg). The colloidal properties of proteins have been investigated by A.G.Pasynskii and V.A.Pchelin; new data have been obtained on the stability of interfacial protein films—models of biomembranes (V.N.Izmailova).

A.I.Rusanov carried out fundamental investigations into the thermodynamics of surface phenomena.

Detailed studies in the colloid chemistry of peat (M.P.Volarovich, I.I.Lishtvan, N.V.Churaev, and N.I.Gamayunov) and coal (R.I.Kucher and V.S.Veselovskii) created a basis for the effective utilisation of these valuable natural raw materials in various branches of technology.

The achievements in colloid chemistry are finding effective applications in many branches of the national economy: in the chemical and petroleum extraction industries, in the food industry, in the synthetic raw and cured rubber industry, in the technology of silicates, plastics, and paint and varnish coatings, in the mining-extraction and mining-chemical industries, in the preparation of lubricating materials and lubricating-cooling liquids, in the related fields of biology, geology, meteorology, medicine, and agriculture, and also in the development of effective measures for the protection of the environment: in water purification, in the trapping of dust in industrial undertakings and mines, and in the fixation and desalination of soilds.

III. ORGANIC CHEMISTRY

Soviet organic chemists have made a large contribution to the development of world organic chemistry. Among the first fields of organic chemistry dealt with during the Soviet period, one should include studies on the chemistry of acetylenic, allene, and diene hydrocarbons, the catalytic reactions of hydrocarbons, the manufacture of synthetic rubber, the chemistry of organophosphorus compounds, and the chemistry of natural products (terpenes and terpenoids, alkaloids, and carbohydrates). Systematic researches have

been carried out in the field of organic synthesis (A.E.Favorskii, N.Ya.Dem'yanov, V.V.Markovnikov, N.D.Zelinskii, S.N.Raformatskii, V.E.Tishchenko, and V.B.Chelintsev) and organometallic chemistry (A.N.Nesmeyanov). Studies have been made on plant and animal products and organic compounds have been synthesised for industrial and medical purposes (tanning agents, plant dyes, alkaloids, and glycosides). These investigations laid the necessary foundations for the development of organic synthetic industry (rubber, plastics, dyes, the processing of petroleum and petroleum products, organic fertilisers, and pharmaceutical products). Subsequently all the main fields of organic chemistry developed successfully on an increasing scale.

1. Physical Organic Chemistry

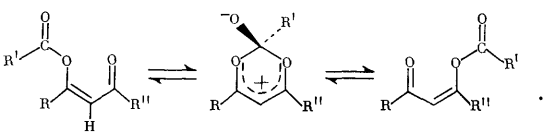
The electronic theory of chemical structure has developed significantly. Relations between the characteristics of the valence state of the carbon atom and the chemical bond parameters have been discovered. In the field of organoelemental chemistry the characteristics of the interaction of various element–carbon bonds with neighbouring unsaturated molecular fragments have been discovered. The characteristics of the structure and chemical properties of non-benzenoid aromatic systems have been studied and quantitative relations have been established between the reactivity and structure of organic molecules. The theoretical foundations for the description of tautomeric phenomena have been extended and new types of tautomeric transformations have been discovered. Hypotheses concerning processes involving the transfer of the reaction centre in which a dual reactivity is clearly manifested have been formulated (A.N.Nesmeyanov, A.E.Arbuzov, B.A.Arbuzov, B.A.Kazanskii, M.I.Kabachnik, and A.E.Porai-Koshits).

As early as 1934, A.E.Arbuzov and A.I.Razumov predicted the possibility of triad phosphoryl–hydroxy-ylide tautomerism, analogous to the keto–enol tautomerism. The phosphoryl–hydroxy-ylide tautomerism has been recently observed in solutions of tertiary phosphine oxides (T.A.Mastryukova, E.I.Fedin, and Yu.T.Struchkov). A new type of tautomerism—the diad phosphorus–carbon tautomerism—has been discovered and investigated.

The tautomerism of many nitrogen-containing heterocyclic systems has been studied by infrared and ultraviolet spectroscopy and the conditions governing the displacement of the tautomeric equilibrium as a function of the nature of the substituent and the solvent have been elucidated (I.A.Postovskii, Yu.N.Sheinker, and I.I.Grandberg). The structure of tautomeric and potentially tautomeric nitrogen-containing open systems has been investigated. Thus the amide–imidol tautomerism has been observed for optically active compounds by spectropolarimetry and the equilibrium in the ketimide–enamine tautomeric system, which had been observed earlier by means of infrared spectroscopy (N.K.Kochetkov and Ya.V.Dombrovskii), was investigated (V.M.Potapov and A.P.Terent'ev). M.M.Shemyakin observed a variety of ring–chain tautomerism involving the amide group and proposed an isotopic method whereby tautomerism can be distinguished from dual reactivity. For example, it has been possible to determine by this method the high rate of tautomeric transformations of diazoaminobenzene, which explains the specific features of the triazene system.

Infrared and Raman spectroscopy (D.N.Shigorin, V.A.Mironov, and Yu.A.Pentin) and high-resolution ^{1}H NMR (E.I.Fedin) have been resorted to in order to account for the nature of the keto–enol tautomerism.

The manifestations of tautomerism in a series of organophosphorus compounds have been discovered and investigated and new types of tautomers have been established: metallotropy, acylotropy, and aroylotropy. The acylotropic tautomerism of the enol acylates of 1,3-diketones has been discovered and thoroughly investigated (V.I.Minkin, Yu.A.Zhdanov, and L.P.Olekhnovich):



Stable enols of sterically unhindered monocarbonyl or organofluorine compounds have been obtained (I.L.Knunyants). In contrast to their non-fluoro-analogues, the energy barrier to the conversion of the stable enols into the keto-form is very considerable. The absence of the tautomerism of these compounds has been established.



Figure 19. Institute of Chemistry of the USSR Academy of Sciences in Gorky.

The phenomenon of the increase of the electrophilicity of weak electrophiles under the influence of strong electrolytes has been studied (N.S.Zefirov and I.V.Bodrikov). This phenomenon, called the Doping effect, has been used to construct novel skeletal structures. New methods for the synthesis of covalent perchlorates and triflates, which are of practical interest for medicine, have been devised.

Procedures for the generation and investigation of the properties and reactions of active intermediate species in organic reactions—radicals, radical-ions, carbenes, carbenoids, carbonium ions, and carbanions—have been proposed. The reactions of stable radicals occurring without the participation of the free valence, have been observed. Computational and experimental methods for the determination of the electronic structures of free radicals, carbenes, and other reactive intermediate species have been created (O.M.Nefedov).

Organic paramagnetic substances belonging to the class of stable nitroxy-radicals have been synthesised and their reactions, proceeding without the involvement of the free valence, have been investigated and theoretical principles of their employment in science and technology have been formulated (M.B.Neiman, L.B.Volodarskii, E.G.Rozantsev, and A.L.Buchachenko).

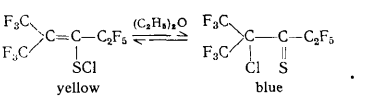
The chemical behaviour of free radicals in the liquid phase has been studied by G.A.Razuvaev. The chain reactions initiated by free radicals, generated by irradiation or thermal decomposition of organometallic compounds, have been studied.

A new field, the metal complex initiation of radical reactions on the basis of Group VI, VII, and VIII metal carbonyls, has been developed (R.Kh.Freidlina). The radical nature of the initiation has been demonstrated and the radicals formed at this stage have been identified. The formation of carbyne and carbide complexes has also been established in the study of the decomposition of the organometallic compounds of tungsten and molybdenum, which results in the formation of carbene species active in the metathetical processes involving olefins and the ring opening reactions of cyclic olefins (B.A.Dolgoplosk). A new type of free radical telomerisation, leading to ω-unsaturated carbonyl compounds which are of practical importance, has been discovered (G.I.Nikishin).

The study of molecular rearrangements is very important for the understanding of the reaction mechanisms and in the search for specific syntheses of compounds with a particular structure. A wide variety of reactions occurring as a consequence of molecular rearrangements have been investigated by E.E.Vagner, S.S.Nametkin, A.E.Arbuzov, A.E.Favorskii, and N.Ya.Dem'yanov.

The transformation of isopropenylcyclobutane into 1,1-dimethylcylopent-2-ene and 1,2-dimethylcyclopent-1-ene, discovered by B.A.Kazanskii, is an interesting example of the Vagner–Nametkin rearrangement. I.N.Nazarov extended the concept of the Favorskii rearrangement to secondary and tertiary polyene alcohols. V.F.Kucherov and M.I.Ushakov discovered a rearrangement of furan derivatives with participation of multiple bonds. The acetylene–allene and allene–diene rearrangements have been found for acetylenic carbinols and halides (T.A.Favorskaya). The reverse allene–acetylene isomerisation has been described by A.A.Petrov. The mechanism of the acyloin rearrangement of α-ketols discovered by A.E.Favorskii has been confirmed by T.I.Temnikova. The rearrangements of α-hydroxyaldehydes into ketoalcohols and α-glycols have been studied by S.N.Danilov and E.D.Venus-Danilova.

The rearrangements of radicals involving the migration of a chlorine atom, the thiyl group, and a hydrogen atom have been discovered (A.N.Nesmeyanov and R.Kh.Freidlina). The phenomenon of chlorotropy has been studied in detail:



The characteristics of electrophilic substitution at a saturated carbon atom have been investigated thoroughly for organomercury and organotin compounds. A polarographic acidity scale for CH acids has been created. The contributions of free ions and ion pairs of different types to the reactions of alkali metal salts of CH acids have been determined and a linear relation has been found between the logarithms of the rate constants for the reactions of carbanions (including ambident anions) and the pK_a of the corresponding RH acids (O.A.Reutov, I.P.Beletskaya, Yu.G.Bundel', and K.P.Butin).

The results of studies of active intermediate species made it possible to achieve a qualitative and in a number of cases a quantitative description of complex organic reactions occurring with their participation and to extend significantly the scope of synthetic organic chemistry. The creation of the method of the "ionic hydrogenation" of organic compounds, characterised by a high selectivity, and of new processes involving carbenes and carbenoids can serve as examples.

A non-catalytic reaction in which the double bonds are hydrogenated by silanes in acid solutions (the ionic hydrogenation reaction) has been proposed. The hydrogenation of thiophens under mild conditions usually gives rise to high yields of thiophanes which are otherwise difficult to obtain and which have important physiological properties (for example, biotin) and antioxidant properties (D.N.Kursanov, Z.N.Parnes, V.N.Setkina, and Z.V.Todres). The ionic hydrogenation reaction has been used, for example, in the synthesis of tetrahydropyrans (promising solvents which do not form peroxides) and in the total synthesis of steroids of the oestrane series (D.N.Kursanov, Z.N.Parnes, G.I.Bolestova, N.M.Loim, M.I.Kalinkin, G.D.Kolomnikova, V.A.Tsyryapkin, Yu.I.Lyakhovetskii, and V.I.Zdanovich).

The mechanism of the oxidative reactions of polymethylated aromatic compounds with electrophiles in strongly acid media has been elucidated. When the reactants are mixed at a temperature between −80° and −100 °C and the system is gradually warmed, the formation of intermediate species can be observed by ^{1}H NMR. Extensive information has been obtained about the mechanisms of the reactions under consideration and convenient methods have been discovered for the preparation of a series of interesting compounds as regards practical applications (for example, 4-methoxy-1,2,5,6-tetramethylphenol and its derivatives tested as stabilisers for certain types of polymeric systems) (V.A.Koptyug).

The method of correlation equations has been used in a large number of studies of reactivities and reaction mechanisms (V.Palm, Yu.A.Zhdanov, A.I.Konovalov, and V.I.Minkin). A correlation equation has been derived for the description, over a wide range of conditions, of reactivities in reactions of practical importance such as the bromination and nitration of aromatic compounds. Correlation equations describing the influence of a substituted heterocycle on the reaction centre and permitting the calculation of the σ constants of the substituents have been found (V.P.Mamaev).

The mechanism of the autoxidation–autoreduction reactions of aldehydes (the Cannizzaro reaction) in alkaline media has been investigated. The alkalinity function, which is a measure of the ability of the medium to ionise a molecule of a weak acid, was used in the analysis of the kinetic data (M.I.Vinnik).

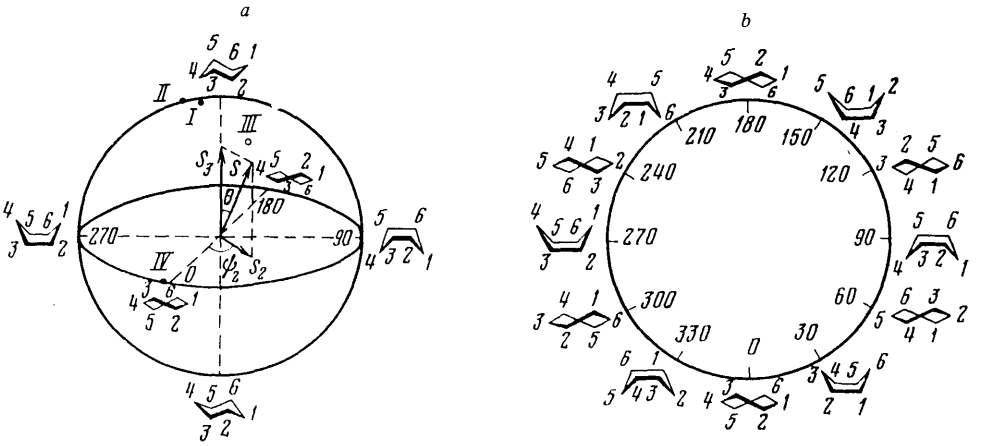


Figure 20. a) Sphere plotted in terms of foldability coordinates for six-membered rings: b) equatorial section through the sphere ($\theta = 90°$).

Significant results have been obtained in the study of the stereochemistry of organic molecules (A.P.Terent'ev and V.M.Potapov). Methods for the determination of the steric structures of molecules with the aid of various physical research procedures have been devised. A method has been proposed whereby the ring conformation can be determined from geometrical data for the molecule and characterised in terms of a minimal number of parameters, the distortion of cyclic molecular fragments can be described quantitatively, and the shapes of the rings in different molecules can be compared (N.S.Zefirov and V.A.Palyulin). Fig.20 presents a sphere plotted in terms of foldability coordinates and representing all possible conformations of six-membered rings.

The phenomenon of the chirality of the nitrogen atom in aziridines has been discovered and studied (S.Hillers and R.G.Kostyanovskii).

Extensive information has been obtained in the field of the stereodynamics of organic molecules. The influence of steric factors on the reaction rates and the possibility of the modification of the direction and rates of reactions under the influence of a high pressure have been studied. Investigations in the field of sterically hindered phenols led to the formulation of new principles for the selection and employment of stabilisers of organic materisl (V.V.Ershov).

The inductive influence of dipolar substituents in inorganic molecules on the polarisability of the surrounding bonds, i.e. on the mobility of their electron clouds, has been observed (B.A.Arbuzov and A.N.Vereshchagin).

The resonance dissociative electron capture by molecules of different types of organic compounds is being investigated by mass spectrometry (S.R.Rafikov, V.I.Khvostenko, and R.G.Kostyanovskii).

Technical means and programmes for generalisations with the aid of computers in the language of structural formulae have been created, which ensures the possibility of the rapid creation of computer data banks of the "structure–property" type and leads to ways of constructing computer systems for the prediction of the properties of chemical compounds and for the design of syntheses (V.A.Koptyug).

2. Organic Synthesis

Fundamental researches into organic synthesis on the basis of petroleum hydrocarbons and their catalytic reactions have been carried out by N.D.Zelinskii. The investigations of the chemistry of acetylenes and cyclic hydrocarbons by A.E.Favorskii served as a basis for the creation of important industrial processes. The researches by S.V.Lebedev, who discovered the fundamental features of the phenomena of the polymerisation of organic molecules and was the first to achieve (in 1931–1932) the synthesis of butadiene rubber on an industrial scale, constitutes a major achievement of Soviet chemical science. I.N.Nazarov investigated the chemistry of acetylene derivatives, in particular vinylacetylene, and synthesised physiologically active substances (promedol and steroid hormones). The study of the chemistry of acetylenic compounds led to the discovery of new possibilities for the preparation of monomers and polymers from acetylene and readily available petrochemical raw material. The superbasic catalysts developed for the first time made it possible not only to intensify many familiar vinylation processes but also to achieve a series of hitherto unknown reactions of acetylene leading to valuable monomers, intermediate products, and reagents (ion-exchange resins, raw rubbers, and epoxy-resins) (B.A.Trofimov).

Higher aliphatic alcohols have been obtained by the oxidation of paraffinic hydrocarbons (A.N.Bashkirov), which served as the basis on which the detergent industry was established. The catalytic reactions of paraffinic hydrocarbons and the chemistry of petroleum products have been investigated by A.F.Plate, R.Ya.Levina, S.R.Sergienko, V.S.Gutyrya, A.M.Kuliev, and I.A.Orudzheva.

In connection with the development of the industry of dyes and medicinal drugs, numerous investigations have been made into the chemistry of aromatic compounds (A.I.Kiprianov). As early as the 1930's, the mechanism of the electrophilic substitution of the benzene ring was determined and the influence of various factors (concentration of sulphuric acid, temperature, and the presence of impurities) on the sulphonation process was elucidated (E.A.Shilov,

V.A.Izmail'skii, A.M.Lukin, B.P.Fedorov, and I.S.Ioffe). The study of the sulphonation of aromatic compounds occupies a major place in the researches of N.N.Vorozhtsov. He has investigated the sulphonation reactions and the nature of the sulpho-derivatives of naphthalene and the influence of various catalysts on this reaction. Industrial methods for the sulphonation of 2-naphthol (I.I.Vorontsov), 2-chloronaphthalene (N.N.Vorozhtsov, Jr.), and an effective method for the vapour-phase sulphonation of benzene (R.K.Eikhman, M.I.Bogdanov and V.N.Ufimtsev) have been developed.

New methods for the preparation of aromatic nitro-compounds have been devised and studied in detail (A.V.Kartashev and A.I.Titov). The nitration of anthraquinones, phenanthrene, acenaphthenes, carbazoles, dibenzopyrenes, and onium compounds has been studied.

The mechanism of the halogenation of aromatic compounds in an aqueous medium has been investigated. The activity series of halogenating agents has been put forward (N.N.Vorozhtsev and V.A.Shilov). The kinetic isotope effects have been determined for the halogenation of aromatic amines, aminoacids, hydroxyacids, and sulphonic acids. The reactivities of alkylating agents in relation to aromatic hydrocarbons have been studied and those suitable for the industrial alkylation of benzenes by olefins in the presence of $AlCl_3$ (N.N.Lebedev) and sulphuric acid (Yu.G.Mamedaliev and M.A.Dalin) have been proposed.

Numerous studies on aromatic diazo-compounds have led to the synthesis of azo-dyes and light-sensitive compounds (V.M.Rodionov, V.K.Matveev, and A.E.Porai-Koshits).

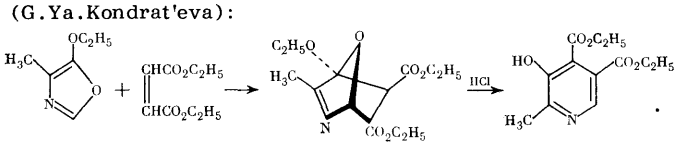
Reactions involving nucleophilic substitution in aromatic compounds have been investigated by A.N.Engel'gardt, P.A.Lachinov, N.N.Vorozhtsov, Jr., D.V.Tishchenko, L.Kh.Freidlin, A.I.Kiprianov, E.Yu.Orlov, S.S.Gitis, and B.I.Stepanov.

In the middle of the 1930's, P.P.Shorygin and A.V.Topchiev began the systematic study of radical substitution in aromatic compounds. The mechanism and the fundamental characteristics of homolytic arylation have been determined by A.N.Nesmeyanov and Kh.S.Bagdasar'yan. Radical arylation with the aid of organometallic compounds has been studied by G.A.Razuvaev. Numerous data on isomeric reactions of aromatic compounds have been surveyed by V.A.Koptyug.

The chemistry of ylide and non-benzenoid aromatic systems has been developed vigorously (D.N.Kursanov, M.E.Vol'pin, V.G.Yashchunskii, Yu.D.Koreshkov, Z.N.Parnes, I.S.Akhrem, Ya.K.Syrkin, and A.A.Bochvar).

The first studies on heterocyclic compounds were carried out by A.E.Chichibabin, V.M.Rodionov, A.I.Kiprianov, I.I.Levkoev, M.M.Shemyakin, V.K.Antonov, and M.G.Voronkov.

The research into the chemistry of heterocycles has now resulted in the synthesis of many effective medicinal drugs, materials for non-silver photography, chemical plant protecting agents, dyes, and other important compounds. These fields are being developed at the institutes of virtually all Union Republics. The synthesis of various heterocyclic systems is developing vigorously. The synthetic possibilities of the Diels-Alder and 1,3-dipolar cycloaddition reactions for the synthesis of new heterocycles have been greatly expanded (B.A.Arbuzov, A.N.Kost, P.B.Terent'ev, A.N.Pudovik, and I.K.Korobitsyna). The employment of oxazoles in the synthesis of a diene system made it possible to devise new methods for the preparation of analogues of vitamin B_6 (G.Ya.Kondrat'eva):



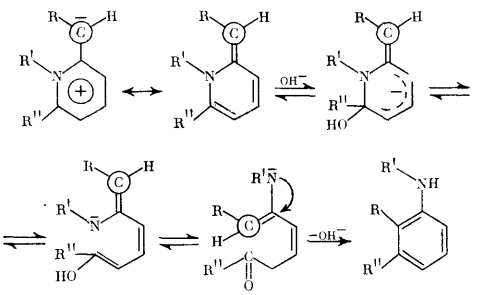
A novel method of synthesis of heterocyclic systems with a wide variety of structures from substituted β-chlorovinyl ketones was discovered by A.N.Nesmeyanov and N.K.Kochetkov. F.Ya.Perveev developed a general method of synthesis of five-membered heterocycles from acetylenic epoxides.

Yu.K.Yur'ev, S.Hillers, A.L.Mndzhoyan, K.Yu.Novitskii, Ya.L.Gol'dfarb, V.G.Yashchunskii, and S.A.Vartanyan have made a major contribution to the development of the chemistry of five-membered heterocycles, azoles, and azines and the study of their reactivity and biological activity.

New methods of synthesis of furan derivatives have been proposed by A.P.Terent'ev: sulphonation by pyridine-sulphonyl trioxide, the synthesis of benzofurans from quinones, and the synthesis of amines of the furan series whose oxidation leads to aminoacids, including optically active aminoacids. N.I.Shuikin investigated the hydrogenation and hydrogenolysis of furan derivatives and also the thermal and catalytic reactions of dihydrofurans.

Six-membered heterocyclic compounds, namely pyrones (R.Ya.Levina, N.P.Shusherina, and L.I.Zakharkin), pyridines (P.B.Terent'ev, I.L.Knunyants, and A.M.Kost), and pyrimidines (V.P.Mamaev and A.L.Mndzhoyan) have been widely investigated.

A new important rearrangement of aromatic heterocycles, namely the recyclisation of pyridinium and pyrimidinium salts, has been discovered (A.N.Kost, R.S.Sagitullin, and S.P.Gromov):



Extensive studies have been carried out on indoles and azaindoles in the search for new physiologically active substances (N.N.Suvorov, L.N.Yakhontov, M.N.Preobrazhenskaya, I.I.Grandberg, and F.S.Babichev). A series of studies on the chemistry of porphyrins have been carried out by R.P.Evstigneeva and G.V.Ponomarev.

New reactions of non-activated heterocyclic substrates and the phenomenon of the dealkylation of sterically hindered tertiary arylamines have been observed. The nature of the influence of the heterocycle and other substituents on the amine–imine tautomerism and the conformation of formazans has been determined. The lactim–lactam, thione–thiol, and azido–tetrazole tautomeric transformations of heterocyclic compounds have been investigated (I.A.Postovskii).

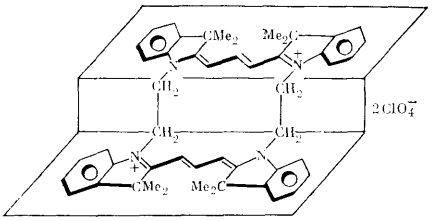
A new oxidation-reduction isomerisation of 1-alkylaminoanthraquinones to derivatives of anthroxazine and the analogous photochemical conversion of 2-alkylaminonapthoquinones into naphthoxazoles have been discovered in recent years (E.P.Fokin). The results of the study of photochemical reactions of alkylaminoquinones have served as a basis for the formulation of a series of new photographic processes and materials.

Preparatively convenient methods of synthesis of acetylpyrimidines as well as a method of synthesis of aminophenylpyrimidines have been devised. A new photochemical reaction involving the addition of pyridine to 9,10-anthraquinone with formation of dihydropyridinoanthraquinone derivatives has been discovered. A method of synthesis of halogenoaminoketones, used as spin labels for biological systems, has

been devised on the basis of nitroxy-radicals derived from imidazoline (V.P.Mamaev). Methods of synthesis of new condensed heterocycles—isoindoles, imidazotriazoles, condensed mesoionic heterocycles, and new types of pyrrole, pyridone, etc. derivatives—have been devised (F.S.Babichev). Comprehensive study of the chemistry of diazocarbonyl compounds made it possible to observe a series of important rearrangements of diazocetyl derivatives of heterocycles and also led to the synthesis of a new type of light-sensitive compound belonging to the class of heterocyclic betaines (V.G.Kartsev).

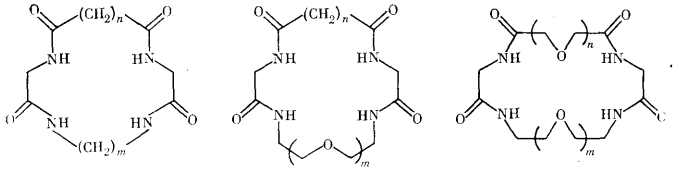
The principles of the construction of six-membered annelated heteroaromatic cations has been formulated, which makes it possible to predict and to carry out experimentally many new chemical reactions of general theoretical importance for organic chemistry (Yu.A.Zhdanov and V.I.Minkin).

A macrocyclic biscyanine, containing two parallel rigidly linked chromophores, namely a bis(1,1'-dimethyleneindolyldicarbocyanine) perchlorate, has been synthesised for the first time:



The possibility of determining the conformations of the chromophores of polymethine dyes from the intensity ratios of the absorption bands of two electronic transitions in the spectra of biodyes has been demonstrated. It has been established that the positions of the boundary energy levels responsible for the colour of the polymethine dyes are described satisfactorily with the aid of three parameters: the length of the polymethine chain and two characteristics of end groups—the effective length and the electron-donating capacity (A.I.Tolmachev).

Much attention has been devoted to the synthesis of macroheterocycles of the type of crown-ethers, cryptands, and similar compounds containing ether, amide, and ester groups and novel methods for the synthesis of these substances have been devised. Macrocyclic tetra-amides, exhibiting interesting complex-forming properties, have been obtained (A.V.Bogatskii and N.G.Luk'yanenko):



The grafting of dibenzo-18-crown-6-ether on silochrome was achieved for the first time and a new heterogeneous reusable catalyst, capable of catalysing a wide range of nuclophilic substitution reactions, was prepared.

The studies on heterocyclic compounds have made a considerable contribution to the development of theoretical ideas in organic chemistry and to the solution of problems involving the creation of new and practically important substances. The scientific developments in the field of the synthesis and study of organic pigments (A.I.Tolmachev), phosphors (B.M.Krasovitskii and I.I.Grandberg), liquid crystals (V.V.Titov), new organic ligands (A.V.Bogatskii and V.M.Dziomko), sensitisers and non-silver photosensitive compounds (V.I.Minkin, V.A.Barachevskii, M.V.Alfimov, K.M.Dyumaev, and V.Z.Kuz'min), corrosion inhibitors (A.V.Fokin), spin labels (M.B.Neiman, E.G.Rozantsev, and A.L.Buchachenko), and reagents necessary for research into the most urgent problems of science and technology (V.M.Dziomko and M.K.Kardoyan) have advanced further.

In the field of biologically active compounds special mention should be made of studies on the development of scientific principles in the search for new effective substances for the prophylaxis and treatment of various diseases.

Studies on the correlations between chemical structure and biological activity have greatly promoted the development of the organic chemistry of medicinal drugs (S.Hillers, I.Ya.Postovskii, V.A.Filov, B.A.Ivin, M.Lidaks, E.Lukevics, and A.B.Rozenblit). These studies, carried out at the borderline beween chemistry, biology, pharmacology, and medicine, made it possible to devise rational approaches to the synthesis of many important medicinal preparations, which have found applications in various branches of medicine. An inter-relation between donor–acceptor properties and physiological activity has been established for a series of compounds containing the phosphoryl group (I.V.Martynov and O.A.Raevskii).

The theory of alkylating metabolites, proposed by L.F.Larionov in the 1950's, led to the creation of effective antitumour alkylating preparations (I.L.Knunyants, V.A.Chernov, M.N.Preobrazhenskaya, E.N.Shkodinskaya, and Z.V.Pushkareva).

A new classification of antitumour preparations in terms of the types of their chemical reactivity has been devised at the Institute of Chemical Physics of the USSR Academy of Sciences. This classification, which is more general than the traditional classification, permits a detailed treatment of the chemical and biological mechanisms of the action of antitumour preparations and also provides a basis for their specific synthesis. Many effective antitumour preparations have been developed at the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR, the Shemyakin Institute of Bio-organic Chemistry, and the Institute of Fine Organic Chemistry of the Academy of Sciences of the Armenian SSR. The specific search for drugs which are pyrimidine derivatives made it possible to synthesise preparations for the treatment of ulcers, epilepsy, and neuralgia (A.L.Mndzhoyan and V.A.Vartanyan) and studies on the chemistry and biological activity of benzodiazepine derivatives led to the synthesis of effective tranquilisers (A.V.Bogatskii and S.A.Andronati).

Hundreds of promising preparations for different purposes are being developed at the present time at the academic institutes alone.

Mention should also be made of the advances in the synthesis and application of the processes and technology for the preparation of products of fine organic synthesis, including medicinal drugs (L.D.Melikadze, M.K.Mardoyan, R.O.Matevosyan, A.A.Brikenshtein, R.Yu.Kalnberga, Ya.V.Melberg, and S.M.Gabrielyan).

Studies on the synthesis of pesticides with different types of activity, consisting of selective chemical poisons which are harmless to man and do not contaminate the environment, are being prosecuted on a wide scale.

Fundamental researches whose aim is to expand the available raw material resources for the preparation of food products are being successfully developed. New ways of isolating pure food products, namely proteins, aminoacids, and carbohydrates which are stable on prolonged storage, have been devised.

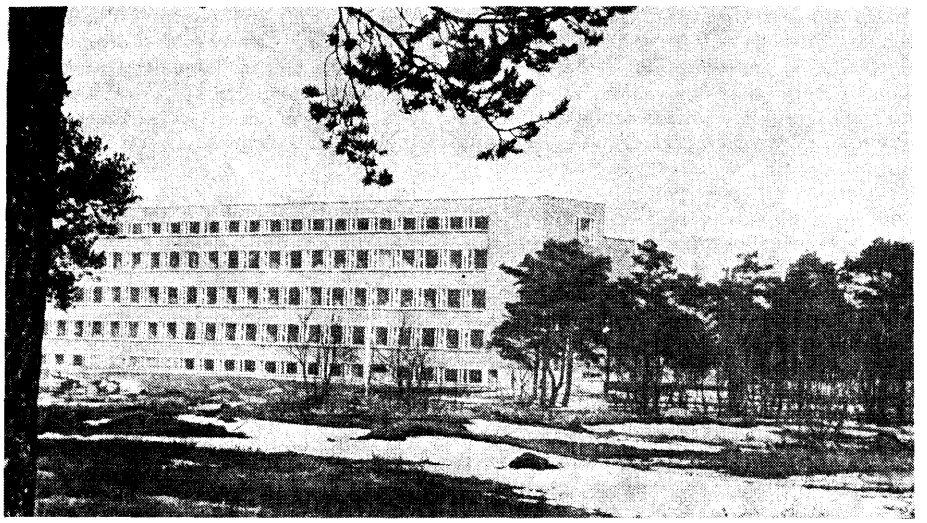


Figure 21. Institute of Chemistry of the Academy of Sciences of the Estonian SSR.

3. The Chemistry of Organoelemental Compounds

The beginning of the development of the chemistry of organoelemental compounds in the USSR is associated with the work of L.A.Chugaev, S.V.Tserevitinov, and V.N.Krestinskii involving the study of organomagnesium synthesis and the subsequent investigations of the mechanisms of the Grignard reactions (A.E.Arbuzov, A.P.Terent'ev, A.D.Petrov, and N.V.Kondrat'ev) and the Wurtz reaction (P.P.Shorygin).

The most important stage in the development of the chemistry of organometallic compounds has been the discovery by A.N.Nesmeyanov (1928) of the diazo-method for the synthesis of organic derivatives of mercury, tin, germanium, arsenic, and other heavy elements:

$$C_6H_5N_2Cl + MCl_2 \rightarrow C_6H_5N_2Cl \cdot MCl_2 \xrightarrow{Cu} C_6H_5MCl + N_2 + 2CuCl\ .$$

The establishment and development of the modern chemistry of organoelemental compounds in which many problems of theory, synthesis, and practical utilisation of these in many ways unique substances are being solved, are indissolubly linked with the name of A.N.Nesmeyanov.

The only Institute of Organoelemental Compounds in the world, named after A.N.Nesmeyanov and run by the USSR Academy of Sciences, has been established in our country.

The initial period of the development of the organic chemistry of Group I and II elements led to the formation of a large number of organic derivatives of lithium, sodium, potassium, magnesium and silver (G.A.Razuvaev, K.A.Kocheskov, I.F.Lutsenko, T.A.Talalaeva, and L.G.Makarova). These studies laid the foundations of the wide-scale application of newly developed methods for the synthesis and utilisation of organometallic compounds in organic synthesis. Organic derivatives of lithium, sodium, and magnesium are nowadays used in all branches of organic synthesis, including the synthesis of natural products.

The characteristics of the formation and decomposition of complexes of metal salts with onium compounds have been determined (A.N.Nesmeyanov and O.A.Reutov).

A.N.Nesmeyanov and D.N.Kravtsev were the first to synthesise metallotropic systems—arylmercury derivatives of nitrosophenols, and discovered the phenomenon of metallotropic tautomerism. As a result of the formulation and development of the dynamic NMR method (E.I.Fedin and Yu.A.Ustynyuk) and the synthesis of new and varied metallogropic systems, in particular keto–enol systems (I.F.Lutsenko and Yu.M.Baukov), the present version of the theory of tautomeric transformations was subsequently established. For non-transition elements, metallotropic tautomerism usually involves the σ,σ migration of a cationoid metal-containing fragment between different coordination centres of one or several ligands. Such rearrangements have been discovered for various Group II–IV elements and for certain other metals.

The search for new metallotropic molecules is being continued at the present time. Such systems have been synthesised, in particular, from aromatic and heterocyclic hydroxy- and mercapto-azomethines with organothallium, organomercury, organoboron, and organogallium migrating groups (V.I.Minkin). Systematic studies are being prosecuted on the kinetics and mechanism of the autoxidation of organometallic compounds and their reactions with organic peroxides. Among the achievements of recent years, mention should be made of the study of the mechanism of the liquid-phase oxidation of allyl derivatives of zinc, cadmium, gallium, and other metals by molecular oxygen. An unusual effect involving inhibition by molecular oxygen of the liquid-phase oxidation of alkyl derivatives of cadmium has been discovered (Yu.A.Aleksandrov). The characteristics of the catalytic addition of aromatic organomagnesium and organolithium compounds to the multiple bonds of enyne systems have been determined (A.A.Petrov). Studies on the chemistry of organoberyllium compounds are being developed (I.I.Lapkin).

The chemistry of organoboron compounds has developed during the last decade as regards synthesis and the study of skeletal structures—carbaboranes, boradamantanes, and boron-nitrogen compounds. Carbaboranes are a new class of stable electron-deficient organoboron polyhedra with unusual properties. After the discovery of the first metal–carbaborane complexes, the study of the organic chemistry of these interesting polyhedral systems has developed.

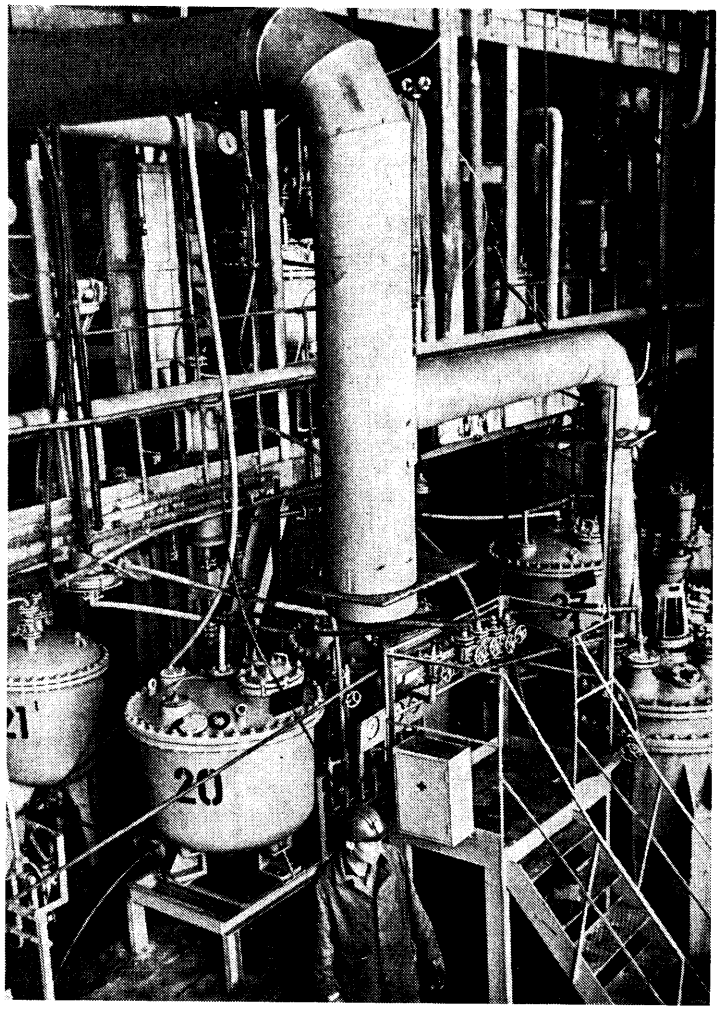
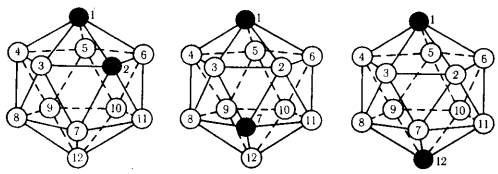


Figure 22. Overall view of the Apparatus Division of the Experimental Factory of the Institute of Chemistry of the Estonian SSR.

Aromatic substitution reactions have been investigated and derivatives containing various functional groups have been obtained.

The thermodynamic stability of carbaborane isomers, which varies in the sequence 1,2-$C_2B_{10}H_{12}$ > 1,7-$C_2B_{10}H_{12}$ > 1,12-$C_2B_{10}H_{12}$, has been studied (L.I.Zakharkin, V.N.Kalinin, O.Yu.Okhlobystin, and V.I.Stanko):

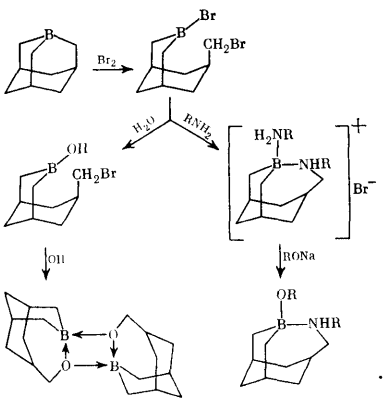


1,2-$C_2B_{10}H_{12}$ *o* 1,7-$C_2B_{10}H_{12}$ *m* 1,12-$C_2B_{10}H_{12}$ *p*

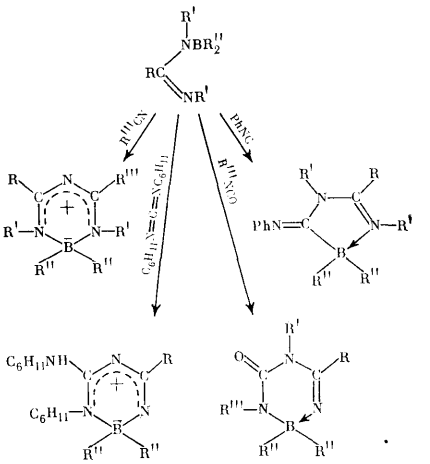
These investigations initiated in their turn a new field in the chemistry of carbaboranes—the synthesis of monomers for the preparation of thermostable carbaborane–based polymers (V.V.Korshak). Carbaborane–silane monomers based on *m*-carbaborane and 2,4-dicarba-*closo*-heptaborane(7), which have found applications in the manufacture of thermostable rubbers, have been synthesised and investigated (A.F.Zhigach). On the other hand, a method of synthesis of metal-containing derivatives or carbaboranes with a B–M σ-bond using the corresponding mercury compounds has been devised (A.N.Godovikov and V.I.Bregadze). This reaction makes it possible to investigate a new class of carbaboranes—σ-metal-carbaboranes.

An interesting field in the chemistry of organoboron compounds is associated with the synthesis of boron-containing analogues of adamantane: 1-, 2-, 3-boradamantanes. The related bicyclic derivatives are being investigated; in particular, the rearrangement of 3-alkenyl-3-borabicyclo[3.3.1]-nonanes to 3-borabicyclo[4.3.1]decane, involving ring expansion, has been discovered (B.M.Mikhailov).

Methods of synthesis of 2-oxa- and 2-aza-borahomoadamantanes have been devised:



Bearing in mind that the boron atom in boradamantanes has a tetrahedral coordination, the successful synthesis of such derivatives must be recognised as an important achievement even in the chemistry of heteropolyhedranes with its numerous exotic aspects. The high antiviral activity of many compounds of this class has aroused additional interest in them. Studies in the field of various boron–nitrogen compounds are also developing successfully (V.A.Dorokhov). Nitrogen-containing heterocycles with a tetracoordinate boron atom have been obtained. Carbaborane peroxides containing an acylperoxy-group at the boron atom of the carbaborane nucleus have been synthesised (O.Yu.Ol'dekop).



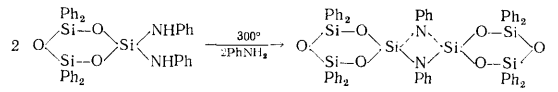
After Ziegler's discovery of reactions involving the addition of various aluminium trialkyls to olefins in the presence of cocatalysts, organoaluminium compounds found extensive applications in industry as catalysts of the polymerisation of olefins. This led to a considerable development of the fundamental research in the field of organoaluminium compounds. The first representatives of a new class of aluminium complexes with alkyl derivatives of alkali metals were synthesised for the first time, an improved method has been proposed for the synthesis of higher normal alcohols from the corresponding dialkylaluminium chlorides, and new general methods for the synthesis of ketones have been devised (L.I.Zakharkin). Procedures have been found for the hydroalumination of linear and cyclic mono-olefins by isobutylaluminium hydride in the presence of zirconium compounds (G.A.Tolstikov). Methods have been developed for the synthesis of non-solvated alkylaluminoxanes and organoaluminoxane-magnesioxanes (N.N.Korneev), which are used in polymerisation reactions of ethylene and the synthesis of raw rubbers and polyisoprene.

On the whole, there is a tendency in the field of organoaluminium compounds towards an expansion of their applications in organic synthesis and polymerisation processes as reactants and catalysts. Their industrial manufacture has become the basis for the development of other branches of chemical industry.

In the field of organosilicon compounds, which have a history longer than one century, organosilicon polymers (polyorganosiloxanes) have been synthesised in our country (K.A.Andrianov). The problem of constructing structures combining the plasticity of organopolymers and the thermal stability characteristic of silicates was solved in this way. Since then the synthesis of organosilicon monomers has become one of the main fields in the chemistry of organosilicon compounds. New methods have been devised for the synthesis of 1,3- and 1,5-divinylorganocyclosiloxanes and dihydrosiloxanes, which are used for the synthesis of cyclolinear polymers with an ordered structure.

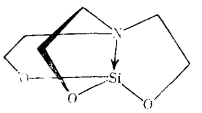
Methods have been devised for the synthesis of epoxides and the di-, tri-, and tetra-merisation of ethynyltrimethyl-(trialkoxy)silanes (G.A.Tolstikov). These studies are being developed in the tradiational close association with industry.

A new field in the chemistry of organosilicon compounds involves the study of the methods of generation, the nature of the double bonding, and the properties of unstable silicon analogues of olefins and other unsaturated compounds. Unstable compounds such as 1,1-dimethylsilaethylene (with an Si=C bond) and 1,1-dimethylsilathione (with an Si=S bond) are investigated. A new method of synthesis of the 1,1,2,2-tetramethyl-1,2-disilacyclobutane monomer has been devised (N.S.Nametkin). Major advances have been made in the study of the chemistry of organocyclodisilazanes. New spiro-compounds with a nodal silicon atom have been obtained (K.A.Andrianov):



Silyl derivatives of furan and silicon-substituted 2,3-dihydrofurans have been synthesised (E.Lukevics).

After the discovery of silatranes



and the observation of their biological activity, a new field, associated with the synthesis of physiologically active substances, has been established in the chemistry of organosilicon compounds (A.N.Pinchuk). A series of studies have been carried out on the chemistry of silatranes (M.G.Voronkov). Effective stimulators of the biosynthesis of proteins and nucleic acids and new medicinal preparations, in particular silatranylalkyl esters of polyfluoroalkanecarboxylic acids with psychotropic activity and low toxicity, have been discovered. New types of insecticides have been obtained—phosphonium salts of the silatrane series. Another class of compounds of pentacoordinate silicon is being investigated, namely aroyloxymethyltrifluorosilanes, whose steric structure has been determined by X-ray diffraction.

The chemistry of organogermanium and organotin compounds is developing. A general method has been proposed for the synthesis of 1-organylmetallotranes of Group IVB metals (K.A.Kocheskov). Monomeric compounds of tin and lead containing metal–nitrogen double bonds were synthesised for the first time. Studies are being made on acetylenic and vinyl derivatives of Group IVB metals. A general method of synthesis of polyethynyl derivatives of tin, based on the interaction of trialkylethynylstannanes with tin halides, has been found. The coupled reaction of acetylenic derivatives involving hydrogenation and combination with lead compounds has been discovered (A.A.Petrov). The catalytic copolymerisation, oligomerisation, and diene synthesis reactions of vinylgermanes have been studied (V.P.Yur'ev). Methods for the synthesis of germanium- and silicon-substituted derivatives of compounds with small rings—cyclopropanes, cyclobutanes, and 2-oxetans—from element-substituted ketens have been devised (I.F.Lutsenko). Covalent organobimetallic compounds containing tin, silicon, and germanium are widely investigated (N.S.Vyazankin). The electronic interactions in compounds of Group IVB elements are being investigated (A.N.Egorochkin).

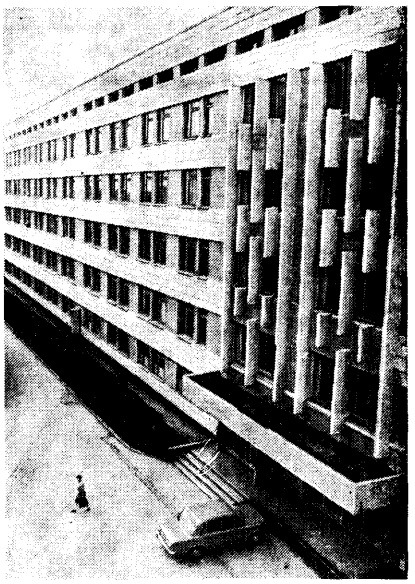
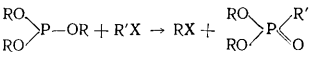


Figure 23. One of the blocks of the Kazan Institute of Chemical Engineering.

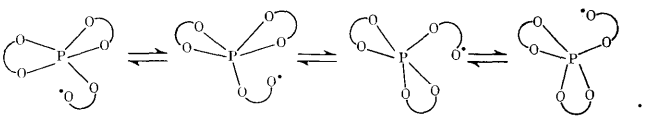
It is noteworthy that in recent years practical applications of organogermanium and organotin compounds have been outlined. Organotin derivatives of the imides of dibasic carboxylic acids have shown a high fungicidal activity and derivatives of maleic and thioglycolic acids reduce the rate of dehydrochlorination of poly(vinyl chloride) and prevent the cross-linking of macrochains (G.A.Razuvaev). New types of biologically active substances, doping additives, adsorbents, and ion-exchange resins have been synthesised from organometallic compounds of Group IVB elements (M.G.Voronkov).

The chemistry of organophosphorus compounds has long traditions in our country. As early as 1905, A.E.Arbuzov discovered a rearrangement of phosphorus acid esters on oxidative interaction with alkyl halides, which A.N.Nesmeyanov called the "highway to synthesis":



Subsequently two leading schools, the Moscow school (M.I.Kabachnik) and the Kazan school (B.A.Arbuzov), converted the field of organophosphorus compounds into the most highly developed branch of organoelemental chemistry.

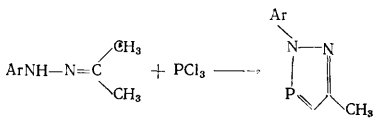
At the beginning of the 1950's, M.I.Kabachnik created a quantitative theory of prototropic tautomeric equilibria. Studies on various tautomeric processes in organophosphorus compounds constitute one of the traditional and fruitful fields. Thus a new combined form of prototropic tautomerism—the phosphorus–carbon diad tautomerism coupled with the triad keto–enol tautomerism—has been discovered recently. A new type of radicalotropic tautomerism, the wandering valence, has been discovered and investigated; this phenomenon has been observed in *ortho*-quinoxy-radicals containing not only phosphorus but also Group I–V elements:



Evidently the free valence "runs around" all the oxygen atoms in the *para*-catechin ligands, so that the effective coordination number of phosphorus is six. The migration of the free valence is accompanied by the dissociation and formation of P–O bonds and the system is therefore in essence a model of an intramolecular radical substitution reaction (M.I.Kabachnik, T.A.Mastryukova, S.P.Solodovnikov, and N.N.Bubnov). The alkylation and acylation of phosphorus ketoimides has been investigated (N.A.Nesmeyanov).

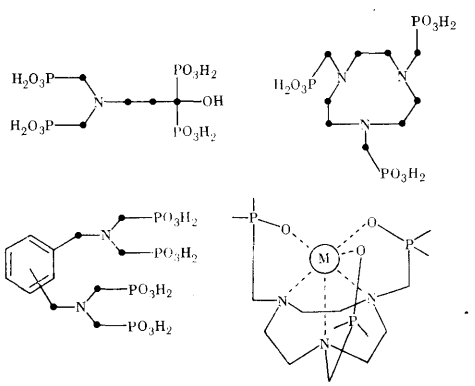
Extensive studies have been made in order to develop methods for the synthesis of organophosphorus compounds. A way of synthesising organophosphorus compounds from phosphorus by the photochemical reaction of elemental phosphorus with *ortho*-quinones has been found (M.I.Kabachnik). The synthesis of new types of substances has been achieved: 1,3-azaphosphetidines, 1,3,5-diazaphosphorinanes, oxoazaphospholans, phosphines, optically active substituted vinyl esters of phosphorus acids, and pentacovalent monocyclic phosphoranes with a P–H bond (B.A.Arbuzov). Methods have been developed for the synthesis of phosphoroisothiocyanatodithioates, hydroxyaminoalkyl phosphorothioates, and the anhydrides of acetoacetic and phosphorothioic acids. New organophosphorus monomers and polymers have been obtained (A.N.Pudovik). New derivatives of phosphorus have been synthesised: acyclic polyfluoroalkoxyphosphoranes, phosphorylated ketens, crown-ethers, aziridines, aminodichlorophosphazoalkanes, and phosphorus ylides with P–C and P–H bonds; compounds of dicoordinate phosphorus have also been obtained: oxazaphospholes with the O–P=N triad and phosphazenes with a glycine ester residue (A.V.Kirsanov, L.N.Markovskii, and A.M.Pinchuk). Phosphorus-containing heterocycles of a new type have been synthesised: triphosphacyclobutanes, cyclic vinyl esters of phosphorus acids, and heterocycles with phosphorus–phosphorus bonds (I.F.Lutsenko).

The phenomenon of the formation of five-membered heterocyclic systems with dicoordinate phosphorus has been discovered (N.N.Mel'nikov, N.I.Shvetsov-Shilovskii, N.P.Ignatova, A.V.Vasil'ev, V.V.Negrebetskii, and L.V.Vilkov):



A new method has been proposed for the synthesis of organophosphorus compounds—by the reaction of chloroethynylphosphonates with electrophiles, nucleophiles, and radical reagents (A.A.Petrov).

Systematic studies are being carried out in the field of organophosphorus complexones, extractants, and sorbents. New polydentate organophosphorus extractants and complex-forming ion-exchange resins, suitable for the selective isolation, purification, and separation of valuable metals, have been obtained (M.I.Kabachnik, T.Ya.Medved', and D.M.Dyatlova):



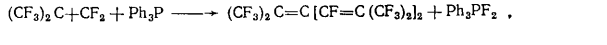
Methods of synthesis of phospholen polymers with sorption activity have been devised (A.N.Pudovik). Ligands with two, three, and four phosphoryl groups have been synthesised and have proved to be effective complex-forming agents in reactions with alkali metals, particularly with Li^+ (I.V.Martynov).

The applied aspects of the chemistry of organic compounds of phosphorus are associated with the synthesis of new physiologically active organophosphorus compounds (M.I.Kabachnik, T.A.Mastryukova, and N.N Godovikov).

The syntheses of many mixed chlorinated esters of dialkylphosphoric acids (B.A.Arbuzov and A.N.Pudovik), dimethyl *N*-allylphosphoramidate, and methyl *N*,*N*-diethylenephosphorimidothioate (E.N.Nifant'ev), and phosphorodithioate esters and phosphoryl- and thiophosphoryl-sulphonamides (N.N.Mel'nikov) have been devised.

The vigorous development of fluorine chemistry was stimulated by the problem of the separation of uranium isotopes which arose at the beginning of the 1940's. Despite being comparatively new, organofluorine chemistry has developed so rapidly that fluorine-containing derivatives have now been obtained for all classes of organic compounds. A school of organic chemists specialising in organofluorine chemistry, headed by I.L.Knunyants, was established in our country (L.S.German, B.L.Dyatkin, Yu.A.Cheburkov, N.P.Gambaryan, I.N.Rozhkov, R.A.Bekker, and K.N.Makarov). The studies of A.V.Fokin, L.M.Yagupol'skii, N.N.Vorozhtsov, and L.T.Eremenko have made a large contribution to the development of organofluorine chemistry.

Methods for the direct fluorination of organic compounds by elemental fluorine in water and methods of synthesis of organofluorine compounds by anodic fluorination have been developed. A new reaction of perfluoroisobutene with triphenylphosphine has been discovered recently:



It leads to the formation of a cross-conjugated triene. Ways of obtaining conjugated perfluoropolyene systems and methods for the synthesis of perfluoroalkyl sulphides and sulphones as well as fluorine-containing alcohols and glycols have been found.

The chemistry of carbanions, namely the anionoid reactions of organofluorine compounds initiated by fluoride ions (KF, CsF), are being widely investigated. The reactions of azaanions derived from perfluoro-2-azapropene or trifluoromethyl isocyanate with electrophiles in the presence of KF or CsF have been studied.

Results of practical value have been obtained in the field of fluorine-containing monomers and polymers. The unique properties of fluoro-plastics—chemical stability, long life, etc.—have led to their incorporation in many branches of technology. A new light-sensitive polymer composition and a photolithographic process based on it have been created using heterocyclic polyfluoro-compounds. New fluorine-substituted aromatic di- and tetra-amines—the initial monomers for polymeric materials—have been obtained (V.P.Mamaev). Plans have been made for semi-industrial plant for the synthesis of various fluoropolymers (S.S.Ivanchev).

Surfactants based on organofluorine compounds (for example, on perfluoroalkanesulphonic acids) have been synthesised. Studies on the preparation of blood substitutes from perfluorocarbon aqueous emulsions with a high oxygen capacity are being actively prosecuted: the syntheses of perfluoro-derivatives of tertiary amines and mono- and di-alkyl-substituted perfluorocycloalkanes have been achieved and the reductive dimerisation reaction of perfluoro-olefins has been discovered.

Fluorine-containing carcinolytic compounds—5-fluorouracil and fluorofur—play an important role in the chemotherapy of tumours (S.Hillers). An industrial method for the direct fluorination of uracil in order to obtain 5-fluorouracil has been devised.

Studies in the field of π-complexes of platinum metals began as early as the 1940's in our country (A.D.Gel'man). However, in fact only since the discovery in 1953 of biscyclopentadinyliron(II) (ferrocene) has the modern period of the development of the chemistry of organic derivatives of transition metals begun. This period is characterised by the continuous growth of our knowledge about the chemistry of π-complexes; new structural types are being discovered in succession, namely π-cyclopentadienyl, π-arene, metal–carbene, and other complexes, and new elements continue to be included in the range of substances investigated. The existing concepts of valence and the coordination number of a metal are being revised and ideas concerning the many-centre nature of the metal–organic ligand bond have been put forward. The chemistry of metal carbonyls is developing and, becoming incresingly intertwined with the chemistry of π-complexes, ensures the interpretation of the "classical", organometallic, and coordination chemical sciences. The role of physicochemical research methods—X-ray diffraction analysis, resonance methods, and mass spectrometry—is increasing.

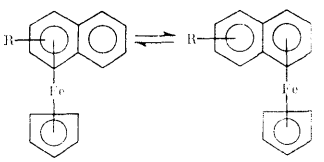
The organic chemistry of ferrocene has developed vigorously. The most important reactions involving electrophilic substitution in cyclopentadienyl ligands have been discovered in relation to ferrocene and its oxidised form—the ferrocenium cation.

A.N.Nesmeyanov's students, namely E.G.Perevalova, V.A.Sazonova, N.S.Kochetkova, M.I.Rybinskaya, S.P.Gubin, N.A.Vol'kenau, and V.A.Nefedov, have made a major conribution to the development of these aspects of the chemistry of ferrocene and other metallocenes. Boron-, copper-, silver, and gold-substituted ferrocene derivatives have been synthesised (V.A.Sazonova and E.G.Perevalova) together with the ferrocenyl derivatives of metallocenes containing Group IVA metals (G.A.Razuvaev and G.A.Domrachev).

Reactions involving substitution in the cyclopentadienyl ligands of manganese and rhenium cyclopentadienyl tricarbonyls have been carried out. The reactions of tolane with vanadium, niobium, and tantalum cyclopentadienyl tetracarbonyls have been investigated (K.N.Anisimov, N.E.Kolobova, and A.A.Pasynskii).

The complexes of Group IVB and VIII metals are widely investigated in the chemistry of π-arene derivatives. Dibenzenechromium, whose derivatives are used to prepare metallic coatings, has been studied (G.A.Razuvaev and G.A.Domrachev). Monoarene chelate complexes of chromium are being studied from the standpoint of the search for systems of the "atom in hydrocarbon cage" type and an arene complex of chromium with three chelate rings and a series of derivatives of the ferrocenophane type have been synthesised (M.I.Rybinskaya). The mechanisms of reactions involving substitution in various π-cyclopentadienyl and π-arene complexes have been investigated (D.N.Kursanov and V.N.Setkina).

The chemistry of π-cyclopentadienyl-π-arene derivatives is being studied and a new type of metallotropic transformations has been discovered (N.A.Vol'kenau and S.P.Solodovnikov):



Metallotropic rearrangements of a similar type (but not degenerate rearrangements of the type $\eta^6 \rightleftharpoons \eta^5$) have been observed for chromium tricarbonyl complexes of fluorene (A.N.Nesmeyanov and Yu.A.Ustynyuk). In both cases the metal-containing fragment undergoes reversible intermolecular π,π migration in the plane of the condensed ligand.

The chemistry of π-acetylenic and π-olefinic complexes has been widely studied in connection with problems of metal complex catalysis (Ya.K.Syrkin, B.A.Dolgoplosk, and I.I.Moiseev). The cationic complexes of the type π-benzene–π-allyltriphenylphosphineruthenium have been studied (A.N.Nesmeyanov) and a series of vinyl complexes with a metal–carbon multiple bond have been synthesised (N.E.Kolobova). The acetylene–allene rearrangement in the chelate π-arene complex of chromium has been observed (M.I.Rybinskaya).

Organometallic complexes with paramagnetic *o*-quinone, phenoxy-, and other ligands are being studied, methods for their synthesis have been devised, and oxidation-reduction transitions, exchange reactions, and other processes are being investigated (E.A.Abakumov and O.Yu.Okhlobystin).

Research into the synthesis of various polynuclear (bridged and cluster) compounds is being carried on. Polymetallic compounds containing polynuclear chains of covalently linked atoms have been obtained: Ge–Hg–P–Sn and Ge–Cd–P–Ge (G.A.Razuvaev and M.N.Bochkarev). The addition of organomercury compounds to zerovalent platinum and palladium complexes has been achieved (O.A.Reutov and V.N.Sokolov).

As fundamental knowledge accumulates, the proportion of applied studies increases. Practical applications have been proposed for many processes developed and substances synthesised. Non-silver photographic materials with a satisfactory resolving capacity and a comparatively high sensitivity have been obtained from ferrocene derivatives and other transition metal complexes (A.N.Nesmeyanov, N.S.Kochetkova, G.A.Shveikhgeimer, G.A.Razuvaev, and G.A.Abakumov). Metallopolymers have been obtained by the thermal decomposition of organometallic compounds in solution in a polymer (Yu.A.Aleksandrov). A method has been devised for the preparation of chromium, molybdenum, and tungsten powders from the corresponding carbonyls for use in the electronic and abrasive industries (V.G.Syrkin).

As early as 20 years ago, G.A.Razuvaev began his studies on metal isolation processes in thermal reactions of organometallic compounds. Systematic researches, designed to form inorganic coatings by the photochemical and thermal decomposition of organometallic compounds in various phases, are being prosecuted nowadays under the supervision of G.A.Razuvaev and G.A.Domrachev.

Transition metal complexes are finding extensive applications in catalysis and for this reason the synthesis of complex organometallic catalysts is one of the most important fields in the chemistry of transition elements and has been developing vigorously since the beginning of the 1950's. As early as 1960, a method was proposed for the oxidation of acetylene with the aid of palladium catalysts (Ya.K.Syrkin, I.I.Moiseev, and M.N.Vargaftik), which found an industrial application. It has been shown in relation to benzene derivatives of molybdenum, tungsten, and rhenium and trimethylsilyl derivatives of niobium, chromium, and cobalt that their decomposition is accompanied by the formation of carbene and carbyne species. These results make it possible to discover new approaches to the study of the elementary steps in catalytic reactions such as hydrogenation, dehydrogenation, and metathesis. Catalysis systems containing compounds of Group IVB elements are being devised for petrochemical synthesis (B.A.Dolgoplosk, E.I.Tinyakova, and K.L.Makovetskii).

A series of active hydroxylation catalysts have been put forward and the mechanism of catalysis based on Group VIII metal complexes has been studied (A.A.Petrov). The factors influencing the mode of hydroxylation of acetylene in the presence of rhodium catalysts have been investigated (M.G.Voronkov). Effective catalysts of the synthesis of 11 heterocycles have been found (G.A.Tolstikov and N.S.Kochetkova). Catalysts of ionic homogeneous hydrogenation are being synthesised (D.N.Kursanov and Z.N.Parnes).

Nickel and palladium complexes of chiral phosphines and phosphites have been used as highly efficient enantioselective catalysts of the cyclodimerisation of 1,3-dienes (G.A.Tolstikov). A highly selective catalyst of the alternating copolymerisation of propene and butadiene has been devised on the basis of vanadium compounds (E.N.Kropacheva).

The catalytic properties of complexes of graphite with certain metals (a kind of heterogenised catalysts) are being investigated. It has been shown that they are effective in the conversion of graphite into diamond.

The development of a new field of metal complex catalysis, for the regulation of vital processes in biochemical systems, has been initiated (M.E.Vol'pin).

Studies designed to create effective cluster catalysts of the dissociation and activation of the C–C and C–H bonds are being prosecuted (I.I.Moiseev and A.S.Berenblyum).

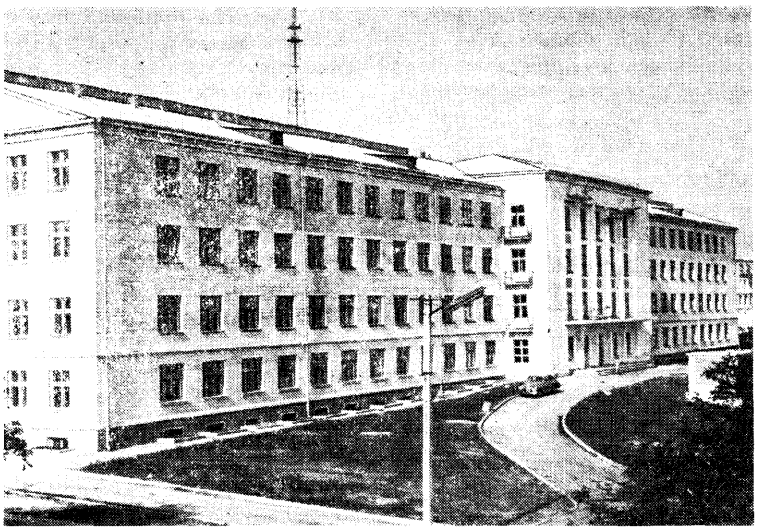


Figure 24. Institute of Chemistry of the Academy of Sciences of the Moldavian SSR.

The search for new initiators of radical reactions based on organometallic complexes of metal carbonyls has been carried on successfully in recent years. It has been shown that iron and manganese carbonyls are effective initiators of radical telomerisation (R.Kh.Freidlina, A.B.Terent'eva, and F.K.Velichko). A new class of radical polymerisation initiators based on transition metal complexes of the type $R_nM.LiCl_4$, where M = Hg, Sn, or Pb, has been recently discovered. Effective initiators of the polymerisation of acrylic monomers have also been proposed on the basis of organometallic peroxides of Group IV–V elements (Yu.A.Aleksandrov).

The advances in the field of synthesis and study of organometallic compounds would have been impossible without an extensive development and application of physicochemical research methods. Among these methods a leading role is usually assumed by X-ray diffraction analysis with the aid of which the structures of many complexes have been elucidated (Yu.T.Struchkov), microwave spectroscopic methods (E.I.Fedin, Yu.A.Ustynyuk, S.P.Solodovnikov, N.N.Bubnov, and G.A.Abakumov), mass spectrometry (D.N.Kursanov and Yu.S.Nekrasov), as well as vibrational spectroscopic methods (V.T.Aleksanyan and B.V.Lokshin). The role of the photoelectron and X-ray electronic spectroscopy is becoming more important and studies are being made of the electronic structures of organometallic compounds by quantum-mechanical methods (N.E.Dyatkina, D.A.Bochkar, and A.A.Levin). Methods for the analysis of organoelemental compounds are being developed (E.E.Gel'man, E.A.Terent'eva, and S.G.Mairanovskii).

4. Bio-organic Chemistry

Bio-organic chemistry is one of the most vigorously developing fields in modern natural sciences. It is associated with the study of the essential chemical features of vital processes and its development has been responsible for advances in biotechnology, medicine, and agriculture. The principal objects of study in bio-organic chemistry are proteins and peptides, nucleic acids and oligonucleotides, carbohydrates, lipids, their various mixed derivatives (glyco-, nucleo-, and lipo-proteins), and subcellular structural elements (biomembranes). Apart from biopolymers, low-molecular-weight bioregulators of the type of hormones, prostaglandins, pheromones, neuropeptides, antioxidants, etc. are also being investigated.

The foundations of bio-organic chemistry were laid in our country as a result of studies which have since become classical, in the chemistry of the most important structural components of animal and plant cells—proteins (N.D.Zelinskii and A.V.Palladin) and carbohydrates (P.P.Shorygin), as well as natural biologically active compounds—alkaloids (A.E.Chichibabin) and hormones (M.I.Ushakov).

The establishment of modern bio-organic chemistry as an independent field of study at the junction of chemistry, physics, biology, and mathematics is indissolubly linked with the work of M.M.Shemyakin on the structure and properties of proteins, peptides, antibiotics, and vitamins. The most significant results in the study of the structural-functional properties of proteins and polypeptides have been obtained using new physicochemical methods for the analysis of the primary structure of proteins and the sequence of the amino-acid fragments in peptides. The application of structural mass spectrometry proved to be particularly promising in this respect (M.M.Shemyakin, Yu.A.Ovchinnikov, and N.S.Vul'fson).

Much attention has been devoted to studies on polypeptides and proteins by physical methods. NMR (B.F.Bystrov), infrared spectroscopy (Yu.N.Chirgadze), optical rotary dispersion (V.T.Ivanov), X-ray diffraction analysis (I.S.Andreeva and B.K.Vainshtein), and the combination of physicochemical methods with theoretical calculations (M.V.Vol'kenshtein and O.B.Ptitsyn) are widely used in conformational analysis. Methods for the investigation of the dynamic structure of proteins and the active centres of enzymes using spin, luminescent, and other labels and probes have been devised (T.I.Likhtenshtein).

G.I.Gol'danskii developed a method for the study of the conformational states of biopolymers by introducing a tritium label into the latter and measuring the parameters of the tritium–hydrogen exchange. The sensitivity of the method makes it possible to detect small (local) changes in structure

which are inaccessible to the optical and other "macroscopic" methods.

Most important studies on the analysis of the aminoacid sequence and structure of proteins have been carried out under the supervision of Yu.A.Ovchinnikov: the structure and topography of visual rhodopsin (Fig.25)† and bacteriorhodopsin—unique proteins responsible for the conversion of the light energy into chemical energy—have been determined, the structure of the leucine-binding protein responsible for chemotaxis in bacteria has been elucidated, and the complete structure of one of the key enzymes in nitrogen metabolism, namely aspartate aminotransferase, has been deduced.

The results of numerous experimental studies permitted a better understanding of the nature of the relation between the chemical structure and biological properties of peptides, which placed on a realistic basis the solution of problems of the specific synthesis of compounds with given properties. For example, a series of studies have been made on the analysis of the structures of complex protein neurotoxins (Yu.A.Ovchinnikov) and novel methods for their total synthesis have been devised (V.T.Ivanov).

Soviet investigators have priority in the development of the chemistry of biologically important atypical peptides, in particular depsipeptides (M.M.Shemyakin and Yu.A.Ovchinnikov). A new method of synthesis of linear and cyclic peptides and depsipeptides involving the incorporation of aminoacyl and hydroxyacil groups in peptide systems has been discovered (V.K.Antonov and A.M.Shkrob).

Methodological studies on the synthesis of aminoacids and peptides have been developed. A new rapid method of synthesis of polypeptides in an aqueous medium without isolation of intermediates (D.G.Knorre) and a new method of synthesis of peptides on a polymeric carrier in solution (L.A.Shukina) have been proposed.

New methods for the total synthesis of physiologically active polypeptide preparations have been devised (Yu.A.Ovchinnikov, V.T.Ivanov, and G.Cipens). The industrial manufacture of insulin, a hormone which is difficult to obtain, has been organised. A method has been found for the separation of hormones from the hypophysis (A.S.Khokhlov) and the technology of the synthesis of oxytocin and angiotensin has been set up (G.Cipens).

Fundamental and applied studies on the establishment of a scientific basis for the synthesis of artificial food, begun on the initiative of A.N.Nesmeyanov, have been widely developed. Methods have been devised for the synthesis of aminoacids, peptides, and proteins by chemical and biological procedures and studies have been made on the chemistry of odour and taste and on the principles of the preparation of new forms of food (V.M.Belikov, S.V.Rogozhin, and R.V.Golovnya).

The first studies on the chemistry of nucleic acids include those involving the determination and comparison of the nucleotide compositions of deoxyribonucleic acids (DNA) in various low and high organic forms [simple and advanced species?] (A.N.Belozerskii). This branch of bio-organic chemistry is directly related to key studies on molecular biology and gene engineering.

Fundamentally new approaches to the determination of the primary structure of transport RNA have been devised (A.A.Baev and D.G.Knorre) and considerable advances have been made in the study of the interrelation between the structure and mechanism of the functioning of DNA. Oligomeric fragments of phage and bacterial DNA have been synthesised and individual genes have been obtained (Yu.A.Ovchinnikov and M.N.Kolosov) and the possible types of aminoacid–nucleotide bonds in nucleotide models have been investigated (M.A.Prokof'ev). The first Soviet apparatus for the automatic synthesis of oligonucleotides has been constructed and successfully tested (D.G.Knorre).

Soviet chemists have significant achievements to their credit in studies on the esterification, oxidation, and degradation reactions of cellulose and other polysaccharides such as glycogen, starch, and dextrans (A.E.Favorskii, S.N.Danilov, M.F.Shostakovskii, Z.A.Rogovin, N.I.Nikitin, and M.M.Ushakov).

Effective methods have been devised for the structural analysis of carbohydrates, in particular a mass-spectrometric method for the determination of the sequence of carbohydrate fragments in oligosaccharides (N.K.Kochetkov and O.S.Chizhov).

The synthetic chemistry of carbohydrates has developed considerably, new methods have been devised for the formation of the glycosidic linkage (G.B.Elyakov, A.Ya.Khorlin, and A.F.Bochkov), as well as procedures for the preparation of *C*-glycosides (Yu.A.Zhdanov). The reactivities of phosphites and phosphinites derived from carbohydrates, which are intermediates in the synthesis of phosphorylated sugars, have been studied (A.A.Petrov and E.E.Nifant'ev).

The studies on the mono- and oligo-saccharides which form part of the composition of biologically important carbohydrate-containing substances are important. N.K.Kochetkov developed methods for the investigation of carbohydrate fragments for the synthesis of structural elements of antibiotics such as erythromycin, oleandomycin, etc. The synthesis of the biologically specific natural *O*-antigenic polysaccharide of the bacterium *Salmonella newington* was achieved for the first time (Fig.26). These results indicate the possibility of the utilisation of artificial antigens in the preparation of monovalent vaccines and can explain at a molecular level the immunological properties of bacteria (N.K.Kochetkov). A new glycopeptide antitumour preparation (blastolysin) has been isolated from the cell membranes of *Lactobacillus*

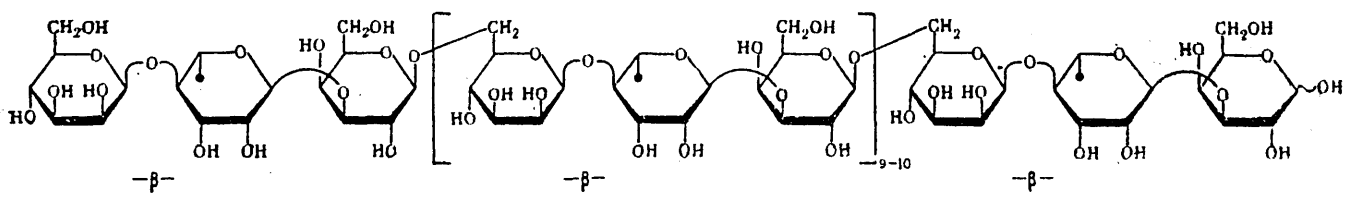


Figure 26. The structure of the oligosaccharide exhibiting the serological activity and specificity of the natural *O*-antigenic polysaccharide of the bacterium *Salmonella newington*.

†This figure was published in the journal "Bioorganicheskaya Khimiya" (Bio-organic Chemistry), 1982, No.10. [It does not appear in the Russian text (Ed. of Translation)].

bulgaricus, characterised chemically and biologically, and proposed for clinical tests (Yu.A.Ovchinnikov and V.T.Ivanov). Treatment of the influenza viruses with detergents led to the isolation of glycoproteins which are the antigens of the influenza virus constituting the basis of the subvibrion glycoprotein vaccine (N.K.Kochetkov).

Considerable advances have been made during the last one and a half decades in the chemistry of lipids and lipotropic biologically important substances (vitamins, hormones, antioxidants, etc.). The characteristics of the composition of lipids in biological membranes in various pathological states have been investigated (E.V.Dyatlovitskaya and E.B.Burlakova) and a new class of lipids based on dihydric alcohols has been discovered (L.D.Bergel'son). Methods for the synthesis of all the principal types of glycerolipids (R.P.Evstigneeva) and spin-luminescence-labelled phospholipids (V.I.Shvets) have been devised. The characteristics of the changes in the antioxidant activity of membrane lipids and their relation with natural antioxidants have been widely investigated (E.B.Burlakova). The studies of K.I.Dyumaev, R.P.Evstigneeva, G.A.Tolstikov, G.I.Dubur, L.D.Smirnov, V.V.Ershov, G.A.Nikiforov, and A.A.Volod'kin have been devoted to the synthesis of natural antioxidants and their synthetic analogues. The research into the chemistry of prostaglandins has been developed (L.D.Bergel'son, K.K.Pivnitskii, J.Freimanis, and Yu.E.Lille).



Figure 27. Institute of Physical Organic Chemistry of the Academy of Sciences of the Belorussian SSR.

The first studies on the chemistry of steroid hormones date back to the 1930's when methods were proposed for the chemical modification of steroids. The Soviet industry of steroid hormones based on cholesterol was created in the postwar period. In the 1950's work on the total synthesis of steroid compounds was begun in I.N.Nazarov's laboratory and was subsequently developed by I.V.Torgov, V.F.Kucherov, S.I.Zav'yalov, and V.I.Maksimov. The microbiological and enzymatic reactions of steroids have been investigated by G.K.Skryabin and N.N.Suvorov.

The modern problems of bio-organic chemistry are also related to the study of the molecular mechanisms of the most important vital processes (immunity, adaptation, and reception) and the development of pathological states. This field is closely adjacent to biochemical, biophysical, and molecular biological studies on the biosynthesis of proteins (A.S.Spirin), cell energetics (V.P.Skulachev), the functioning of proteins as biological catalysts (S.E.Severin), and various kinds of regulatory activities (E.S.Severin).

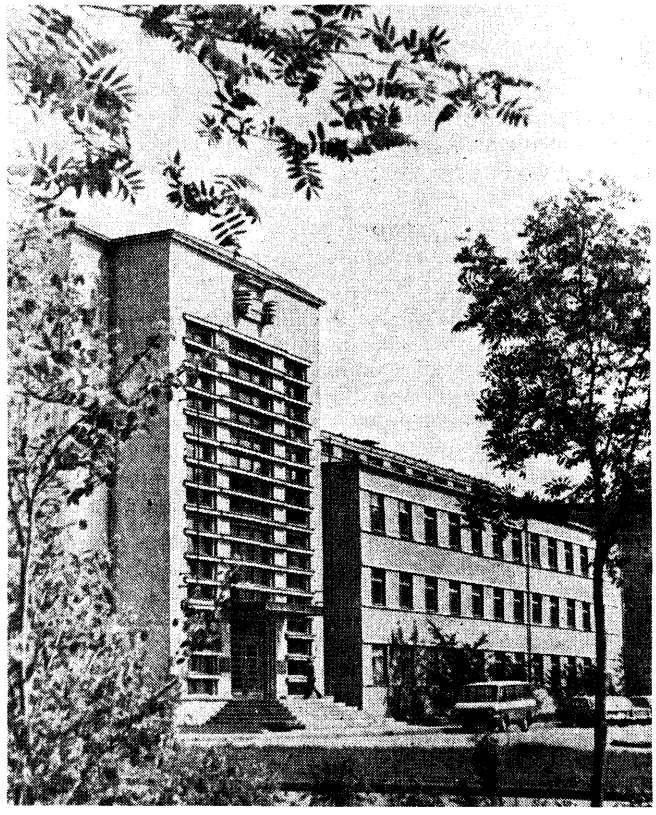


Figure 28. Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR.

Soviet scientists have priority in the discovery of the key stages in the mechanisms of nitrogen metabolism (A.E.Braunshtein), muscle contraction (V.A.Engelhardt), photosynthesis (A.A.Krasnovskii), and nitrogen fixation (M.E.Vol'pin and A.E.Shilov). Studies on cytochrome P-450 (A.A.Akhrem and A.I.Archakov), peroxidase, and erythrocuprein (G.Kh.Bunyatyan)—the enzymes designed to protect the cell from harmful exogenic and endogenic factors—are being actively prosecuted.

The advances in the chemistry of natural products together with those in the organic chemistry of a wide variety of different classes of compounds constitute the basis of the important field of the chemistry of medicinal drugs and biologically active compounds.

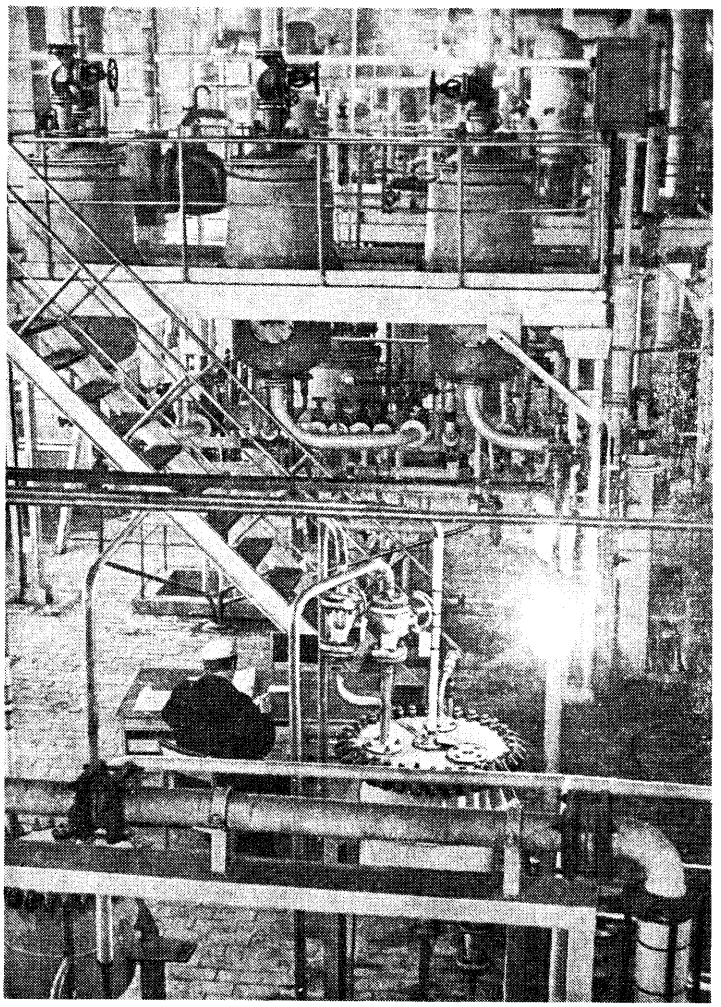


Figure 29. One of the workshops of the experimental factory of the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR.

The modern antibiotics industry, producing all the most important antibiotics, has been established in the USSR. The most important chemical investigations of antibiotics include the discovery and determination of the structure of chloramphenicol and its derivatives (M.M.Shemyakin), the synthesis and investigation of the mechanism of the action of cycloserine (N.K.Kochetkov, R.M.Khomutov, and M.Ya.Karpeiskii), the determination of the absolute configuration of tetracyclines (M.N.Kolosov), the development of methods for the synthesis of penicillins and their analogues (I.L.Knunyants, I.T.Strukov, and S.Hillers), the development of general methods for the separation of mixtures of streptotkricins (A.S.Khokhlov), and the synthesis of new Soviet antibiotics of the anthracycline and pyrimidotriazine series (G.F.Gauze and S.M.Navashin). The recently developed free-radical semiquinone type mechanisms of the chemical and enzymatic reduction of a large series of antitumour antibiotics are of considerable interest (Fig.30); the dependence of the selectivity of the action of the antibiotic on its redox potential, the oxygen potential, and the acid–base properties of the medium has been established (G.N.Bogdanov, V.V.Luzhkov, and V.S.Orlov).

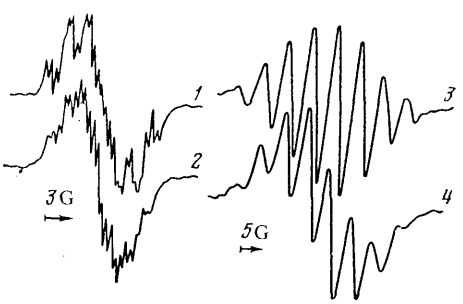


Figure 30. EPR spectra of the free radicals formed in the chemical reduction of carminomycin (curve *1*), rubomycin (curve *2*), and reumycin (curve 3) and in the enzymic reduction of reumycin (curve *4*).

A large group of medicinal preparations are substances of plant origin, in particular alkaloids, whose chemistry has been dealt with in the studies of A.P.Orekhov, N.A.Preobrazhenskii, A.S.Sadykov, and S.Yu.Yunusov.



Figure 31. Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences.

The use of organic paramagnetic compounds belonging to the class of stable nitroxy-radicals for the chemical modification of alkylating agents, antimetabolites, and antibiotics constitutes a fundamentally new trend in the synthesis of combined-action anticancer preparations. Quantum-chemical and quantum-biological methods have led to new procedures in the specific synthesis of highly efficient medicinal preparations.

The prospects for the further development and coordination of research in bioorganic chemistry are determined by the resolution of the Central Committee of the Communist Party of the Soviet Union and the Council of Ministers of the USSR entitled "The Further Development of Physicochemical Biology and Biotechnology and the Utilisation of Their Achievements in Medicine, Agriculture, and Industry" (1981). This programme, which provides for fundamental studies on the physicochemical principles of vital activity, is designed, to create with the aid of biotechnological methods, new medicinal agents, preparations for agriculture, and food products.

5. Petrochemistry

The start of systematic studies on the chemistry of petroleum is associated with the names of D.I.Mendeleev, V.V.Markovnikov, F.F.Beil'shtein, N.D.Zelinskii, M.I.Konovalov, N.M.Kizhner, K.V.Kharichkov, S.S.Nametkin, and L.G.Gurvich. A series of specialist research organisations were set up during the first years of Soviet rule. An extensive network of petrochemical establishments, including the institutes and branches of the USSR Academy of Sciences and the Academies of Sciences of the Union Republics, branch research institutes, and a series of higher educational establishments is at present active in the USSR. Industrial undertakings have played an important role in the incorporation of new petrochemical processes in industry (D.V.Ivanyukov and S.V.Lemaev).

The most important trends in the development of petrochemistry are determined by the problems of modern petroleum processing and petrochemical industries. Among these are the study of the chemical composition and properties of petroleums, the creation of scientific foundations for petroleum processing in order to obtain a wide assortment of petroleum products and lubricating materials, the development of processes for the synthesis of high-octane components and hydrocarbon monomers (ethylene, propene, butadiene, isoprene, styrene, acetylene, and others) for the manufacture of polymers, rubbers, and fibres, and the synthesis of hydrocarbon derivatives with functional groups and technically important products—additives to oils and fuels, surfactants, solvents, and auxiliary substances for the processing of polymeric materials.

The extensive and planned study of the chemical composition of Soviet petroleums was begun by S.S.Nametkin and his coworkers at the end of the 1920's; with the aid of physical and chemical methods, the compositions of petroleums and natural gases from many deposits in the Soviet Unions and also of the principal petroleum processing products were investigated. The specific synthesis of model hydrocarbons was an important field of study (N.D.Zelinskii, A.F.Plate, A.D.Petrov, R.Ya.Levina, and A.L.Liberman). Synthetic hydrocarbon standards constituted the basis of a "combined method" for the study of straight-run petrols (B.A.Kazanskii and G.S.Landsberg). After 1960, a new stage of the research into the properties of hydrocarbons, characterised by a wide-scale employment of physical (particularly chromatographic and spectroscopic) methods for the determination of the composition and structure of the components of petroleum products, was begun (A.V.Topchiev, N.M.Kusakov, G.D.Gal'pern, P.I.Sanin, A.F.Plate, S.R.Sergienko, and A.A.Petrov).

The compositions and properties of petroleums and condensates from a series of industrial deposits, including new deposits in Western Siberia, Turkmenia, and Kazakhstan, were characterised. A new scheme for the chemical classification of petroleums in the Soviet Union has been proposed. A data bank for the compositions and properties of the petroleums of the USSR is being created (G.N.Bol'shakov). Heteroatomic compounds (sulphur, nitrogen, oxygen, and metal-containing compounds) have been identified and their contents determined; new ways have been found for the isolation and utilisation of these compounds. High-molecular-weight components of petroleum have been widely investigated. A new group of fossil hydrocarbons have been discovered: cyclanes with an isoprenoid aliphatic chain and isoprenoid alkanes (Yu.K.Yur'ev, R.D.Obolentsev, I.Ya.Postovskii, G.D.Gal'pern, I.U.Numanov, V.G.Ben'kovskii, S.L.Gusinskaya, N.K.Lyapina, A.A.Petrov, and A.A.Polyakova).

Model thiophanes, necessary for the identification of the thiophanes in sulphur-containing petroleums of the USSR, have been synthesised and investigated spectroscopically (Yu.K.Yur'ev). The decomposition reactions of the thiophen and thiophane rings, which constitute the basis of the industrial desulphurisation of petroleums, have been studied.

Native asphaltenes and hybrid paraffino-cycloparaffin structures have been investigated in the petroleums of Western Turkmenia. Procedures have been proposed for the rational utilisation of the tar-asphaltene component of petroleum. The efficiency of the combined thiocarbamide complex-formation and separation methods for the determination of the structures of high-molecular-weight fractions has been demonstrated (S.R.Sergienko and A.S.Eigenson). The composition of highly viscous Caspian Region petroleums of Kazakhstan has been studied and a technological scheme for their processing has been developed (N.K.Nadirov).

A series of studies have been performed on the utilisation of fractions of naphthenic hydrocarbons from petroleum, on the preparation of synthetic naphthenic acids, and on their application in various branches of the national economy (B.K.Zeinalov and A.M.Niyazov). Among the new syntheses, mention should be made of the synthesis of methyladamantanes containing 1–4 methyl groups (P.I.Sanin and E.I.Bagrii) and of unsaturated sulphides of the benzene, naphthalene, thiophen, and benzodifuran series (E.A.Viktorova).

The interactions of variable valence metal complexes with hydrocarbons and non-hydrocarbon compounds from petroleum have been investigated, which made it possible to put forward a novel method for the purification and improvement of the quality of petroleum products. Catalytic systems have been created for the elimination of mercaptans from petroleums and for the decomposition of hydrogen sulphide to elemental sulphur (N.S.Nametkin and V.D.Tyurin).

A photochemical method has been devised for the isolation of ash-forming elements from petroleums and petroleum products in the Georgian deposits. The ability of polycyclic aromatic hydrocarbons to sensitise the photochemical oxidation of naphthenic hydrocarbons in mineral oils has been demonstrated.

In the field of the inter-reaction of hydrocarbons, fundamental studies have been carried out on leading processes in petroleum processing: on thermal and catalytic cracking, on pyrolysis, on extensive hydrogenation processing of petroleum, and on the improvement of the quality of petroleum products.

During the first years of Soviet rule, the studies of V.N.Ipat'ev, N.D.Zelinskii, A.F.Dobryanskii, B.V.Byzov, M.D.Tilicheev, A.D.Petrov, S.N.Obryadchikov, A.N.Sakhanov, and N.A.Butkov made a large contribution to the development of the theory and practice of cracking. Subsequently Soviet investigators laid the scientific foundations of the thermodynamics, kinetics, and mechanism of the thermal cracking of hydrocarbons and carried out extensive studies on the cracking of heavy petroleum products in order to obtain motor fuels. The thermocatalytic reactions of individual hydrocarbons became one of the main subjects of academic research. B.A.Kazanskii, M.G.Gonikberg, and A.E.Gavrilova investigated the influence of high pressure on the rate of the thermal and catalytic cracking of alkanes. A.D.Stepukhovich proposed a mechanism of the cracking reactions and a theory of the chain decomposition of paraffinic hydrocarbons. The kinetics, thermodynamics, and technology of the high-temperature processing of saturated hydrocarbon gases were investigated by K.P.Lavrovskii and A.M.Brodskii.

The employment of the tracer atom method made it possible to determine the dependence of the hydrogen concentration on the composition of the mixtures pyrolysed and to discover the elementary steps which determine the nature of the mutual influence of hydrocarbons during their pyrolysis (K.P.Lavrovskii and R.A.Kalinenko).

Significant advances have been made in the field of the mathematical modelling and the optimisation of thermal cracking processes; the methods and apparatus for these processes have been improved. A new high-temperature procedure for the processing of pyrolytic tar by its repeated pyrolysis, which ensures the preferential formation of aromatic hydrocarbons, has been proposed. The scientific principles and schemes for the combined processing of liquid pyrolysis products of petroleum hydrocarbons in order to isolate styrene, cyclopentadiene, and methylcyclopentadiene and also to obtain polymeric petroleum tars have been established (G.M.Mamedaliev, K.P.Lavrovskii, and N.S.Nametkin).

Promising methods for the pyrolysis of hydrocarbons and other organic compounds in fused metallic media and in electric discharges, designed to obtain acetylene, carbon black, ethylene, and other products (N.S.Pechuro) and also procedures for catalytic pyrolysis (Ya.M.Paushkin and S.P.Adel'son), have been devised. Different versions of the high-speed thermocatalytic pyrolysis, permitting an effective processing of various hydrocarbons in order to obtain motor fuels and monomers, have been developed (V.S.Aliev).

The mechanism of the high-temperature (above 1000 °C) hydrodealkylation of toluene has been determined and it has been shown that the reaction proceeds via the formation of methylcyclohexadienyl radicals with their subsequent decomposition into benzene and the methyl radical (Yu.A.Kolbanovskii).

Chemical reactions which are carried out in a plasma jet at 2000–3000 °C proved to be promising for the synthesis of many important chemical products (L.S.Polak). The scientific principles of many plasmachemical processes for the preparation of acetylene and technical hydrogen from natural gas, unsaturated hydrocarbons from liquid petroleum products and crude petroleum, and the synthesis gas for the manufacture of vinyl chloride have been determined. The industrial application of these processes in many chemical combines has been achieved.

Catalytic cracking, which is widely employed at the present time, was initiated in the studies of V.N.Ipat'ev, S.V.Lebedev, and L.G.Gurvich devoted to the reactions of hydrocarbons and oxygen-containing compounds in the presence of aluminosilicate catalysts. Subsequently studies of the mechanism and kinetics of catalytic cracking, of the reactions constituting this complex process, and of the nature of the aluminosilicate catalysts were carried out by A.V.Frost, A.V.Topchiev, Yu.G.Mamedaliev, M.F.Nagiev, A.A.Petrov, K.V.Topchieva, G.M.Panchenkov, V.S.Gutyrya, and V.S.Aliev.

The development of research into the thermal catalytic reactions of hydrocarbons led to the introduction of the hydrogenation processing of petroleum fractions, tars, and individual hydrocarbons (N.D.Zelinskii, V.A.Kazanskii, N.M.Karavaev, I.B.Rapoport, A.D.Petrov, B.K.Klimov, A.V.Lozova, A.F.Plate, M.S.Nemtsov, D.I.Orochko, V.I.Karpov, and I.V.Kalechits). The scientific principles of the processes involving the synthesis of artificial liquid fuel and catalytic processes leading to the improvement of the quality of petroleum products and the preparation of high-octane components and monomers, namely aromatisation, reforming, isomerisation, and dehydrogenation of hydrocarbons, have been determined.

The catalytic dehydrogenation of C_6 and higher paraffins has been discovered (B.L.Molgavskii, V.I.Karzhev, B.A.Kazanskii, and A.F.Plate), which made it possible to synthesise aromatic hydrocarbons from readily available paraffinic hydrocarbons.

In order to obtain synthetic rubber monomers (butadiene, isoprene, and styrene) from the corresponding paraffins and olefins, studies have been made on the catalytic dehydrogenation of n-paraffins, n-olefins, and ethylbenzene (A.A.Balandin, M.Ya.Kagan, B.A.Kazanskii, Yu.G.Mamedaliev, N.I.Shuikin, S.R.Sergienko, and V.S.Aliev).

The study of the alkylation of aromatic and paraffinic hydrocarbons, undertaken in view of the need to synthesise high-octane components of motor fuel, was begun in the 1920's by V.N.Ipat'ev, N.A.Orlov, and G.A.Razuvaev and was then developed simultaneously in many scientific establishments. Problems of the synthesis of benzene homologues using various catalysts have been investigated by A.V.Topchiev, Yu.G.Mamedaliev, M.A.Dalin, Ya.M.Paushkin, and V.I.Isagulyants.

The fundamental studies on the catalytic reactions of hydrocarbons, carried out by N.D.Zelinskii, B.A.Kazanskii, and A.A.Balandin, served as a basis for the development of the theory of hydrogenation and dehydrogenation catalysis and for the development of many processes of practical importance.

Highly effective and selective catalysts, in particular catalysts for the hydromethylation of toluene and the dehydrogenation of hexane, for the synthesis of benzene, and for the dehydrogenation of ethylbenzene and styrene have been devised. Studies have been made on the mechanisms of the dehydrocyclisation of C_6–C_8 paraffins and olefins. The dehydrocondensation in the catalytic formation of tars and charcoals has been investigated (M.G.Gonikberg, M.I.Rozengart, I.I.Brusov, G.M.Marukyan, and G.V.Isagulyants).

An economical process for the manufacture of butadiene by the single-stage dehydrogenation of butane in the presence of an alumina–chromium oxide catalyst has been devised (O.D.Sterligov). A palladium–zeolite catalyst for the isomerisation of hydrocarbons, a zeolite catalyst for the alkylation of benzene by olefins, and catalysts with added lanthanide oxides, which are active in the hydrogenation and dehydrogenation processes and do not lead to skeletal isomerisation, have been proposed (Kh.M.Minachev).

Zeolite-containing catalysts for cracking in the matrices of natural and modified gumbrin and clinoptilolite as well as catalysts for the isomerisation of aromatic alkyl-substituted hydrocarbons have been developed (L.D.Melikadze and E.M.Benashvili).

A new nickel–aluminosilicate catalyst based on zeolites has been designed for the synthesis of branched C_5 and C_6 hydrocarbons which constitute the raw material for the manufacture of isoprene and a high-octane component of petrol.

Promising procedures for the industrial dehydrogenation of olefins and the hydrogenation of dienes and dicyclodienes in the presence of membrane catalysts, which make it possible to carry out in a single reactor two reactions at high rates and with high yields, have been devised. Membrane catalysts for the practically important hydrodealkylation reactions of alkyl-substituted aromatic hydrocarbons and the isomerisation of alkanes have been found (V.M.Gryaznov and V.S.Smirnov).

A fundamentally new method for the preparation of various types of unsaturated compounds by the coupled dehydrogenation reaction involving a radical-chain mechanism has been proposed (T.M.Nagiev).

Polyfunctional polymetallic cracking, reforming, hydrocracking, and aromatisation catalysts, permitting an increase of the yield of the required petroleum processing products, have been developed (N.K.Nadirov).

An inhibition procedure has been used for the dehydrogenation of butane, isobutane, n-butenes, and isopentenes in order to suppress side reactions and to increase the yield of the required products (P.A.Kirpichnikov).

A thermal catalytic method for the deasphaltisation of heavy oil tar, whereby the yield of the distillate fractions can be increased to 70%, has been developed.

The study of the interconversions of hydrocarbons with the aid of metal complex catalytic procedures has been expanded in recent years. Novel catalytic systems have been devised for the synthesis of poly-*cis*-buta-1,4-diene. New possibilities for stereospecific catalysis have been discovered. In order to obtain valuable chemical products, in particular new monomers, the dimerisation, codimerisation, oligomerisation, and co-oligomerisation reactions of unsaturated hydrocarbons are being widely investigated in the presence of metal complex catalysts (B.A.Dolgoplosk, V.A.Kabanov, G.A.Tolstikov, B.A.Krentsel', V.M.Vdovin, V.S.Aliev, V.S.Gutyrya, and V.Sh.Fel'dblyum).

New homogeneous highly selective catalysts have been found for the oligomerisation of olefins and 1,3-dienes and also a catalytic system for the dimerisation of ethylene to *trans*-but-2-ene (Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences).

Systems for the metathesis of α-olefins and silicon-substituted olefins, based on silica gel and a series of organo-elemental transition metal complexes fixed on various mineral and organic carriers, have been proposed and investigated (M.E.Vol'pin, B.A.Dolgoplosk, and Yu.I.Ermakov).

The synthesis of hydrocarbon derivatives with functional groups or petrochemical synthesis proper constitutes the most extensive branch of petrochemistry as regards the number and variety of the reactions employed and the products and intermediates thus obtained. Derivatives with functional groups are employed by the petrochemical industry for its own needs primarily as the raw material for the synthesis of monomers in the large-scale manufacture of polymers.

Methods for the synthesis of olefins and dienes from available oxygen-containing compounds were proposed by V.N.Ipat'ev in relation to the catalytic dehydration of alcohols. S.V.Lebedev suggested and developed an effective process for the conversion of ethanol into butadiene. These studies played a decisive role in the establishment of the industrial manufacture of synthetic rubber for the first time in the USSR in 1931–1932.

On the basis of the procedure for the preparation of isoprene from acetone and acetylene discovered by A.E.Favorskii, V.S.Kucherov developed a method for the continuous synthesis of pure isoprene suitable for stereospecific polymerisation. At the beginning of the 1940's, N.D.Zelinskii and A.L.Klebanskii synthesised vinylacetylene and then divinylacetylene and its homologues.

An effective industrial method for the synthesis of isoprene from isobutene and formaldehyde has been created on the basis of studies carried out under the supervision of M.S.Nemtsov and M.I.Farberov.

The manufacture of raw rubbers with improved stability at high and low temperatures and in corrosive media has developed in recent years on the basis of results of studies of the synthesis of organosilicon monomers (K.A.Andrianov and A.D.Petrov) and fluorinated unsaturated compounds (I.L.Knunyants, V.A.Ponomarenko, S.V.Sokolov, and V.S.Shpak).

Polyurethane rubbers and also polyethylene and poly(propylene glycols) obtained from monomers containing an epoxy-ring have exceptionally good qualities. The epoxidation of olefins by peracids constitutes the basis of a familiar method of synthesis of epoxy-derivative of olefins proposed by N.A.Prilezhaev. In recent years studies on this reaction have been developed by M.S.Malinovskii.

The world production of epoxypropane is at present largely based on the catalytic epoxidation of propene by organic hydroperoxides. This process is being investigated by

M.A.Dalin, B.R.Serebryakov, A.G.Liakumovich, and Kh.E.Khcheyan.

The synthesis of epoxyethane by gas-phase catalytic oxidation has been converted into an industrial process and has been provided with a theoretical basis in the studies of M.I.Temkin. A new highly productive system for the carrying out of exothermic reactions made it possible to increase significantly the rate of the process and the yield of the desired products in the oxidation of ethylene and other hydrocarbons.

The synthesis of acetaldehyde, vinyl acetate, and alkyl ketones by the homogeneous catalytic oxidation of olefins in the presence of platinum and palladium complexes has been the subject of the investigations by Ya.K.Syrkin, I.I.Moiseev, and Kh.E.Khcheyan. In recent years heteropolyacids have been used successfully as catalysts of these reactions (G.K.Boreskov and K.I.Matveev). A major branch of modern petrochemical synthesis consists in the study and practical execution of the carbonylation of unsaturated hydrocarbons (oxo synthesis) with formation of saturated aldehydes, acids, and amides (D.M.Rudkovskii, Ya.T.Eidus, Ya.Yu.Aliev, A.L.Lapidus, and N.S.Imyanitov).

The liquid-phase oxidation of hydrocarbons and their derivatives has been widely studied by S.S.Nametkin, P.I.Moshkin, N.I.Chernozhukov, K.I.Ivanov, P.G.Sergeev, A.N.Bashkirov, V.V.Kamzolkin, V.K.Tsyskovskii, B.K.Zeinalov, and many other investigators. Ultimately extensive theoretical data were obtained and several technological processes for the oxidation of hydrocarbons were proposed for application in practice.

A novel process for the synthesis of phenol and acetone by the oxidation of isopropylbenzene to the hydroperoxide with subsequent heterolytic decomposition of the hydroperoxide was first achieved in the USSR. Isopropylbenzene also serves as the source of an important monomer—α-methylstyrene (P.G.Sergeev).

A.N.Bashkirov and V.V.Kamzolkin demonstrated the validity of, developed, and widely applied the principle underlying the regulation of the liquid-phase oxidation process by introducing into the system the so-called stop reagents—substances ensuring the conversion of the reactive intermediates into stable products in relation to the oxidation of the given compound. Using this principle, new processes were devised for liquid-phase oxidation with enhanced selectivity: of C_{11}–C_{18} paraffins to higher secondary alcohols, of cyclohexane to cyclohexanol, and of isoparaffins to secondary and tertiary alcohols; procedures have also been devised for the synthesis of unsaturated alcohols, glycols, and epoxy-derivatives of olefins.

Using the method involving the oxidative ammonolysis of aromatic hydrocarbons, paraffins, and chloroalkylbenzenes, single-stage syntheses of valuable nitrogen-containing intermediates—nitriles, dinitriles, and imides—have been developed (S.D.Mekhtiev, B.V.Suvorov, T.N.Shakhtakhtinskii, and M.A.Dalin).

New highly efficient catalysts have been devised for the oxidative ammonolysis of hycrocarbons and for the synthesis of many aromatic nitriles, which serve as a basis for refractory fibres, impact-resistant plastics, and important chemical products (R.G.Rizaev and T.N.Shakhtakhtinskii).

Single-stage syntheses of higher primary, secondary or tertiary alkylamines and diamines by the reductive amination of oxygen-containing compounds have been developed (A.N.Bashkirov and G.A.Kliger).

The studies on the halogenation of petroleum hydrocarbons, initiated by V.V.Markovnikov, have been developed as regards chlorination in the studies of A.V.Topchiev, N.I.Shuikin, Yu.G.Mamedaliev, and B.A.Krentsel'. The hydroxychlorination of ethylene with formation of vinyl chloride in a single-pulse adiabatic compression has been achieved (Yu.A.Kolbanovskii). A new technology of the joint synthesis of allyl chloride and chlorine, which is one of the stages of the balanced manufacture of epichlorohydrin and glycerol, has been established. The chloropropene derivative formed as waste in the manufacture of glycerol are converted into tetrachloroethylene by means of oxidative chlorination (T.G.Alkhazov).

The synthesis of fluorohydrocarbons, studied by I.L.Knunyants, A.V.Fokin, and their coworkers, was considered in the section "Organoelemental Compounds".

The study of the nitration reactions of hydrocarbons was begun by M.I.Konovalov and S.S.Nametkin and was then continued by P.P.Shorygin, A.I.Titov, A.V.Topchiev, V.P.Alaniya, S.S.Novikov, M.I.Usanovich, and V.Ya.Shtern.

Processes involving the synthesis of surfactants, additives to lubricating oils, and the starting materials for the latter are extremely important in the petrochemical synthesis of technically useful products. The problems of the synthesis of surfactants have been dealt with by N.S.Nametkin, A.D.Petrov, A.N.Bashkirov, G.I.Nikishin, S.I.Faingol'd, and M.A.Gershenovich. Among these investigations, mention must be made of the application and improvement of the method for the oxidation of paraffins and aliphatic acids, as well as the synthesis of higher aliphatic alcohols from the corresponding ethoxy-derivatives, alkyl sulphates, and alkyl arenesulphonates. The studies on the synthesis of additives to lubricating oils, initiated by S.S.Nametkin and continued by P.I.Sanin and A.M.Kuliev, have undergone a significant development in recent years. Metallopolymeric additives, ensuring an improved resistance of lubricating materials to thermal oxidation, have been prepared (V.A.Proskuryakov).

New antioxidants and corrosion inhibitors for petroleum products as well as new antimicrobial additives for the biological protection of petroleum products against damage by micro-organisms have been developed (A.N.Ivanov, A.M.Kuliev, P.I.Sanin, and E.D.Radchenko). Methods have been devised for the preparation of a series of new chlorine-containing inhibitors and additives to fuels and oils by the hydroxychlorination of petroleum fractions (M.M.Guseinov).

The scientific foundations of the technology of the synthesis of high-quality lubricating oils on the basis of mineral petroleum oils and the products of the oligomerisation of α-olefins and of the alkylation of aromatic hydrocarbons have been laid and the technology has been laid.

The development of the method of synthesis of lubricating oils from sulphur-containing petroleums has advanced up to its industrial application (E.D.Radchenko). Polyfunctional additives to motor and boiler fuels derived from petroleum products have been developed and a large assortment of transmission, hydraulic, and energetic oils has been created.

The branch of petroleum synthesis involving the catalytic syntheses of hydrocarbons and alcohols from carbon and hydrogen oxides has developed vigorously in recent times. The mechanisms, kinetics, and catalysts of these syntheses have been widely investigated by Kh.M.Minachev, A.N.Bashkirov, Ya.T.Eidus, A.Ya.Rozovskii, Yu.B.Kagan, S.M.Loktev, and A.L.Lapidus.

6. The Chemistry of Solid Fuels

The science of fuels was established in our country with participation of outstanding investigators such as I.M.Gubkin, S.S.Nametkin, N.P.Chizhevskii, A.A.Skochinskii, L.M.Sapozhnikov, Yu.A.Zhemchuzhnikov, N.M.Karavaev, A.B.Chernyshev, G.L.Stadnikov, and A.F.Dobryanskii. The Coke

Chemistry Commission, headed by A.E.Porai-Koshits and N.M.Karavaev, supervised the studies designed to supply with raw material the developing organic synthetic industry and participated in the investigation of the possibility of increasing the assortment of chemical products for organic synthesis on the basis of the processing of various types of coal.

A classification of different types of coal was developed, which made it possible to differentiate coals into energy fuel and the raw material for the manufacture of high-quality coke and chemical products and materials.

A theory of the formation of coke from coal mixtures was developed. The studies of L.M.Sapozhnikov on the thermal decomposition of coals and the formation of the plastic coal mass altered radically the ideas concerning the action of various factors on the structural transformations of coal substances.

Theoretical studies of the genesis of coals made it possible to establish the mechanism of the geobiochemical processes involving the conversion of plants into different types of coal. A chemical theory of the formation of bogheads and of the mixed humus-sapropellic origin of coals has been proposed (G.L.Stadnikov).

The scientific foundations of coal petrology have been laid (Yu.A.Zhemchuzhnikov, I.I.Amosov, and I.V.Eremin). A project for a petrological-geochemical classification of mineral coals, based on their genetic parameters, reflecting their molecular structure, composition, and natural characteristics, has been set up. The classification makes it possible to predict the suitability of coals for use in various types of technological processing of solid fuels.

The compositions of coals from different deposits are being analysed in various institutes of our country using modern analytical and physical methods (infrared spectroscopy, EPR, and chromatomass-spectrometry). The polymeric structure of the main organic material in coals and the nature of the humic substances have been established (V.I.Kasatochkin and L.L.Nesterenko).

Much attention is being devoted to the important problem of the synthesis of liquid fuel and of valuable products from coal. The scientific principles have been established and the existing and new technologies of the hydrogenation of coal are being improved and developed respectively. As a result of the use of active catalysts, hydrogen-donating solvents, and polymerisation inhibiting additives, the required hydrogen pressure was reduced from 300–700 to 100 atm. A method of the joint hydrogenation of coal with high-sulphur petroleum, which results in a yield of ~50% of boiler fuel and a considerable amount of motor fuel, phenols, benzene, and other products has been devised (A.A.Krichko and A.P.Lozovoi).

A new class of complex heterogeneous catalysts of the hydrogenation of coal based on transition metal salts of oxoacids has been discovered (V.I.Spitsyn and E.A.Buketov).

Studies have been made on the synthesis of heterogeneous catalysts based on molybdenum and cobalt and used in the hydrogenation of coal. The characteristics of the conversion of the organic mass of coal in the presence of different initiators of the liquefaction of coal have been investigated. Recommendations have been made concerning the application of locally produced catalysts instead of imported catalysts in the hydrogenation of pyrocondensate to benzene (A.A.Krichko and Yu.G.Kambarov).

Research is being conducted on the improvement of methods for the classification of coals and further syntheses based on CO and H_2 using new reactors, catalytic systems, and heat from high-temperature nuclear devices (S.D.Fedoseev, V.P.Struminskii, and Kh.M.Minachev).

Methods have been devised for the so-called energotechnological and energochemical processing of solid fuel (A.B.Chernyshev and Z.F.Chukhanov). Procedures are being developed for the oxidative processing of coals, peat, and shale using di- and poly-carboxylic acids (I.I.Lishtvan, T.A.Kukharenko, and A.S.Fomina).

Studies in the field of conversion of coals into coke are being developed. The existence of successive macrokinetic stages in the conversion of coal substances in the course of their degradation has been established (M.G.Sklyar and G.N.Makarov).

A method has been proposed for the catalytic hydrogenation of coals in the absence of solvents, which yields products soluble in organic solvents (L.M.Litvinenko and S.N.Baranov).

The kinetics of the thermal decomposition and oxidation of brown coals of the Kansko-Achinsk deposit have been investigated and it has been shown that these processes have a free-radical mechanism and that the paramagnetic centres formed in them are stable radicals (A.F.Lukovnikov).

The characteristic features of the distribution of rare elements and non-ferrous metals in coals have been studied (A.Z.Yurovskii and V.N.Ratynskii) and the technology of the preparation of concentrates of rare elements from coal and coal products has been devised and introduced.

It has been shown that heterogeneous coals can be regarded as petrographically composite materials. The scientific principles of the selection of carbonaceous fillers based on coals and anthracites for the electrode industry have been developed (N.N.Shipkov and G.B.Skripchenko). A technology of the large-scale manufacture of constructional materials (porous fillers and an effective constructional ceramic) from the waste in the coal enrichment processes has been created and applied in practice (M.Ya.Shpirt).

The composition of shale from different deposits, whose age is up to one thousand million years, is being analysed and a classification of the aliphatic structural elements of the organic matter [in shale?] has been established. The studies on the catalytic hydrogenation of shale in the presence of an organic solvent and its conversion on reaction with water have demonstrated the likely usefulness of the processing of shale in order to obtain a raw material for the chemical industry and for the synthesis of liquid fuel (I.R.Klesment).

New methods for the industrial conversion of fuel shale into tars, gas, and other products are being devised and introduced (V.A.Proskuryakov, G.A.Lastovkin, and E.F.Petukhov).

Combined methods for the processing of Carpathian menilite shale for the manufacture of asphaltoconcretes, ruberoid, as well as cellular material and special thermoinsulating articles used in the manufacture of precision instruments have been developed and introduced in the national economy (I.L.Grinberg).

The nature and properties of peat and methods of its utilisation in the national economy are being investigated. The ion-exchange properties and the kinetics of the thermo-oxidative and oxidative degradation of peat have been studied; the influence of the cationic composition of peat on the formation of its structure and on the properties of its surface have been demonstrated. This made it possible to develop the scientific principles for the extraction of active sorption materials from peat, for its application in the elimination of gaseous, solid, and liquid contaminants from the environment, for the trapping of non-ferrous metal ions, surfactants, and petroleum products, and for the preparation of catalysts and metal–carbon fibres (I.N.Lishtvan, P.I.Belkevich, and V.E.Rakovskii).

Methods have been proposed for the preparation of new physiologically active feed additives—sugared peat, peat–distillery grain waste feed mixture, and the peat–amido-concentrate feed additive.

The rules governing the specific alteration of the agrochemical properties of peat have been discovered and a technology has been developed for the industrial manufacture of complex granulated fertilisers. A technology of the preparation of protein–vitamin feed and growth substances from peat has been developed and tested on an experimental industrial scale.

7. The Chmistry of Wood

Wood is a promising type of renewable raw material for chemical processing and for the preparation of very important materials, in the first place cellulose, paper, cardboard, and cellulose esters for the polymer industry.

The chemistry of wood began to develop particularly rapidly in our country during the last decades. A.Kalnins played the most important role in this research. Studies have been made on the structure of the woody tissue, the submicroscopic structure of the cell walls, the distribution of the principal components in the cell walls, their alteration in the delignification processes and as a result of other chemical, biochemical, and physical influences, and the role of these changes in the formation of cellulose and other products obtained from wood (V.S.Gromov). Processes involving the formation of the supermolecular structure of the components of wood and their functions are being investigated. It has been demonstrated that wood can be justifiably regarded as a cross-linked polymer whose properties depend on the number of cross-links in the cell walls (P.Erins).

The transformations of wood as a result of chemical, enzymic, mechanical, and thermal treatments, in particular the specific thermolysis of wood and lignin waste, are being investigated (A.I.Kiprianov and A.N.Kislitsyn).

Methods for the preparation of cellulose from wood are being improved and the kinetics and mechanisms of these processes are being studied. Particular attention is being devoted to the creation of new procedures for the delignification of wood whereby cellulose and other products have been obtained without contaminating the environment, in particular oxidative delignification methods (Yu.N.Nepenin, Yu.G.Butko, M.A.Ivanov, B.A.Bogomolov, and V.M.Reznikov).

The structure and properties of hemicelluloses, whose content in wood reaches 30% by weight, and their chemical reactions are being investigated. This will permit an improvement of the technological processes for the synthesis of furfural, the protein-vitamin feed yeast, and other products valuable for the national economy. New types of thermostable fibrous and film materials with specific sorption and catalytic properties for use in the new technology are being developed (M.S.Dudkin and A.I.Usov).

V.N.Sergeeva is investigating the processes involved in the conversion of natural lignin and the activation of technical lignins by chemical and enzymatic treatment. The conversion of natural lignin in the nitric acid digestion of wood in order to obtain cellulose has been studied; the synthesis of new active derivatives of hydrolytic lignin and lignosulphonates, namely oligoesters and rigid foam-polyurethanes for use in the furniture industry, have been developed; a series of ligno-organosilicon compounds with improved thermal stability and plasticity have been synthesised. The processes involved in the enzymic conversion of technical lignins for the preparation of additives in the feed of animals and birds from non-food raw materials are being investigated. The nature of this component and the mechanism of its conversion in technological processes are being considered. The search for ways of utilising lignin is being continued by M.I.Chudakov, E.I.Chufina, and B.D.Bogomolov.

The oxidation of lignin via an electrophilic mechanism with hydrogen peroxide in the presence of catalysts has been investigated and the principles of a single-stage highly selective method for the delignification of wood in order to obtain cellulose have been developed on this basis.

An important branch of the chemistry of wood comprises methods for the preparation of various valuable substances from it. The phenolic compounds in the bark, needles, and wood of the conifers of Siberia and the Far East have been investigated. Methods are being developed for the extraction of resinous substances and the preparation of phytocides and protein-vitamin concentrates.

The physicochemical principles of the preparation of concentrated solutions of cellulose in binary organic solvent–nitrogen tetroxide systems have been studied and coagulation conditions for the formation of modified cellulose hydrate fibres, films of the type of cellophane and cuprophane, and semipermeable film membranes have been determined (F.N.Kaputskii).

The theoretical principles of the industrial technology of this new class of polymeric materials have been deduced; the technological process has been achieved in a series of chemical and cellulose paper undertakings of the USSR (E.L.Akim).

The theoretical principles and a technology of the industrial manufacture of more than 20 types of composite cellulose materials and synthetic paper, some of which have been introduced in industry, have been developed.

The new theoretical approach, based on the hypothesis of differential catalysis, led to the specific alteration of the mechanism of furfural formation of the hydrolytic degradation of pectosans; this made it possible to solve for the first time in world practice the problem of the complete utilisation of the entire polysaccharide complex of deciduous wood in its two-stage processing with formation of sugars, which are subsequently converted into feed yeast. The new technology has been adopted for industrial use. The degree of utilisation of the raw material increases under these conditions from 20 to 80% and the amount of waste is reduced by a factor of three (N.A.Vedernikov).

The study of the vacuum thermal decomposition of wood and other cellulose-containing materials has become the basis of the creation of a new method for the processing of plant materials with formation of levoglucosan as the main product. The polymerisation of levoglucosan and its ethers has been achieved; this resulted in the formation of branched and high-molecular-weight linear polysaccharides with film-forming properties as well as a series of copolymers with epichlorohydrin, oxacyclobutane, and tetrahydrofuran. Thermostable foam polyurethanes, films, and adhesive compositions have been obtained on the basis of levoglucosan and its ethers (O.P.Golova and R.Ya.Pernikis). Unsaturated polyfunctional levoglucosan oligomers, capable of three-dimensional polymerisation, have been synthesised and the products have been used to prepare dense-network polymers with improved hardness and thermal stability and subject to only a small shrinkage.

Hydroxyl-containing oligoethers have been synthesised under V.P.Karlivan's supervision from the waste product formed in the digestion of cellulose—tall oil, which is used to synthesise rigid foam polyurethanes for refrigeration technology and building.

Prostaglandins, which had been previously found only in animals, have been discovered in the living tissues of the larch and the poplar. Prostaglandins have been isolated for the first time from plant tissues and identified and their identity with the prostaglandins isolated from the semen liquid

in warm blooded animals and man has been demonstrated. These studies have led to the discovery of new sources of important biologically active substances (E.D.Levin).

IV. MACROMOLECULAR COMPOUNDS

The establishment of the science of polymers as an independent branch of chemistry dates back to the beginning of the XXth century. The first studies in this field in our country were carried out by the organic chemists A.M.Butlerov, I.P.Ostromyslenskii, P.P.Shorygin, I.L.Kondakov, and A.A.Krakau. The investigations of S.V.Lebedev of diene and allene hydrocarbons were important for the establishment of modern ideas about polymerisation, particularly anionic polymerisation. Lebedev was the first to develop a method for the synthesis of butadiene rubber in 1932 and to organise its industrial manufacture, which was the first in the world.

Fundamental research into polymerisation processes has been developing successfully. As early as the 1930's, S.S.Medvedev was the first to demonstrate the free-radical nature of the active centres in the chain propagation process initiated by peroxides and formulated the concept of chain transfer. In subsequent years studies by this school made a considerable contribution to the development of the kinetic theory of radical polymerisation in bulk (Kh.S.Bagdasar'yan and A.D.Abkin).

The discovery by B.A.Dolgoplosk of oxidation-reduction initiation served as the basis for the development of industrial emulsion polarisation processes in the synthesis of rubber. New ideas about the mechanism of emulsion polymerisation were introduced by the discovery of the phenomenon of the fragmentation of monomer drops under the influence of an emulsifying agent, which plays a significant role in the formation of polymer–monomer particles. The use of combinations of ionogenic emulsifying agents, playing the role of fragmenting agents, with other low-molecular-weight compounds (alcohols and amides) permitted polymerisation at a high rate and at reduced concentrations of the emulsifier and the preparation of highly stable concentrated lattices of various polymers (A.N.Pravednikov and I.A.Gritskova).

The kinetics and mechanisms of anionic polymerisation have been investigated and the influence of the nature of the alkali metal on the composition and structure of the polymers formed has been established (S.S.Medvedev, A.R.Gantmakher, A.A.Korotkov, and B.L.Erusalimskii).

S.S.Medvedev, A.R.Gantmakher, and B.L.Erusalimskii investigated the mechanism of the polymerisation of many unsaturated compounds in the presence of cationic catalysts. The specific features of the cationic polymerisation of rings were investigated (N.S.Enikolopov, S.G.Entelis, and E.B.Lyudvig).

The stereospecific synthesis of poly-1,4-*cis*-isoprene was achieved for the first time in the USSR (A.A.Korotkov). A.V.Topchiev, N.M.Chirkov, G.A.Razuvaev and their students made a major contribution to the study of the processes in the stereospecific polymerisation of olefins. The studies of B.A.Dolgoplovsk and E.I.Tinyakova established the role of the initial metal compounds in complex catalysts and proposed several new catalytic systems, including *n*-allyl complexes for the stereospecific polymerisation of diene hydrocarbons. The chain character of the polymerisation of cyclic olefins with ring opening and the carbene mechanism of reactions of this type were discovered.

The studies of the mechanisms of the equilibrium and non-equilibrium polycondensation (K.A.Andrianov, S.N.Ushakov, V.V.Korshak, S.R.Rafikov, L.B.Sokolov, and S.V.Vinogradova) led to the discovery of the influence of the accompanying reactions and the process conditions on the average molecular weights of the products and their molecular weight distributions. The researches of V.V.Korshak, I.L.Knunyants, Z.A.Rogovin, A.N.Nesmeyanov, R.Kh.Freidlina, and A.A.Strepikheev laid the foundations of the industrial manufacture of polyamides and aromatic polyesters. The study of the polycondensation of diols and polyols and dibasic acids in the presence of unsaturated monobasic acids (A.A.Berlin) led to the creation of a new method of synthesis of polymerisable oligomers with terminal or regularly repeated reactive groups (method of condensation telomerisation).

B.A.Zhubanov investigated non-equilibrium polycondensation and obtained a series of new thermostable polymers based on polyamidoacids, polyheteroarylenes, polyesters, etc.

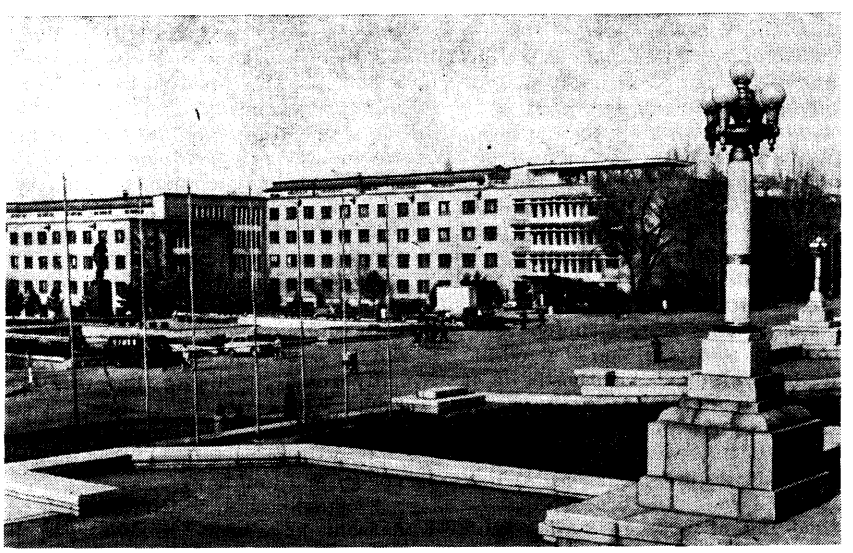


Figure 32. Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR.

Methods of synthesis of polymers have been devised: oxidative dehydropolycondensation, polydiazotisation, polycoordination, and polycyclisation, which made it possible to obtain highly thermostable polymers with a system of conjugated aromatic and heterocyclic rings and possessing semiconducting and catalytic properties (V.V.Korshak, A.M.Sladkov, A.A.Berlin, B.I.Liogon'kii, M.I.Cherkashin, B.A.Krentsel', B.E.Davydov, I.L.Kotlyarevskii, and Ya.M.Paushkin).

N.S.Enikolopov and A.A.Zharov observed that, under conditions of shear at ultrahigh pressures, polymerisation and certain polycondensation processes proceed at enormous rates and these phenomena were studied in detail.

The possibility of the influence of complex-forming agents on the rate and direction of the elementary steps in chain initiation, propagation, and transfer in radical polymerisation was established; this initiated a new chapter in the study of polymerisation processes—the complex-radical polymerisation (V.A.Kabanov, V.P.Zubov, and Yu.D.Semchikov).

The characteristic features of the non-inhibited and inhibited heterophase polymerisation of polyfunctional monomers and oligomers have been studied up to advanced stages of the reaction (G.P.Gladyshev, G.V.Korolov, and N.M.Tvoroegov). These studies laid the foundations for the development of industrial processes involving the synthesis and modification of many polymeris materials.

Investigations of the polymerisation reactions of monomers adsorbed on a surface served as the basis for a novel method of encapsulating friable materials (A.N.Pravednikov and A.D.Abkin).

The modification of the properties of polymers, composite materials, and finished articles made from them is one of the most important fields of the chemistry and physics of macromolecular compounds.

One of the most important types of modification of polymers is the vulcanisation of raw rubbers—a process known already in the past century and still playing a decisive role in the manufacture of rubber. B.A.Dogadkin and his students made a significant contribution to the study of the characteristics and mechanisms of the vulcanisation of raw rubbers.

Compositions comprising oligomers with raw rubbers and thermoplastics have been devised and new industrial methods for the manufacture and modification of rubbers, elastomers, reinforced plastics, hermetically sealing compounds, and other polymeric materials have been developed (A.A.Berlin, A.S.Kuz'minskii, G.N.Petrov, and M.S.Akutin).

Procesess involving the modification of cellulose by grafting, cross-linking, and partial substitution of functional groups, the activation of cellulose, and its etherification reactions have been studied (Z.A.Rogovin, S.N.Ushakov, S.N.Danilov, and Kh.U.Usmanov). The copolymers based on hydroxyethylcellulose, hydroxypropylcellulose, and carboxymethylcellulose are in essence a new type of high-molecular-weight polymeric materials, which will probably find applications in the petroleum, chemical, cellulose-paper, and other branches of industry as thickening agents for aqueous solutions, agents reducing hydrodynamic resistance, and flocculants (M.M.Koton).

The mechanisms of the chemical reactions of polymers under the influence of radiation (degradation and cross-linking) have been investigated and a series of procedures have been proposed for the radiation-chemical modification of polymeric materials (V.L.Karpov). A low-discharge plasma has been used for the treatment of the surfaces of polymer coatings in the preparation of dielectric materials for thin-film condensers and in the development of a method and technology of the deposition of protecting anticorrosion and optically transparent coatings for reflecting surfaces (Ya.M.Kolotyrkin and N.N.Tunitskii).

Since the creation of the polymer industry in our country, studies were begun on the ageing processes of polymers and the development of methods for the stabilisation of polymers and polymeric materials (S.V.Lebedev, G.A.Razuvaev, S.R.Rafikov, M.B.Neiman, K.B.Piotrovskii, and B.M.Kovarskaya).

During the recent decades, these studies have been carried out on a large scale at the Institute of Chemical Physics of the USSR Academy of Sciences. The kinetics of radical-ionic and molecular reactions, constituting the basis of the ageing and stabilisation of polymers, have been investigated in order to devise methods for the regulation of the stability of polymeric materials and articles made from them and for predicting their useful life. Numerous experimental studies have been made on the kinetics and mechanisms of the non-inhibited and inhibited thermo-oxidation of polyolefins and the copolymers based on them. The critical concentrations of antioxidants and the critical mixture compositions have been discovered and synergistic phenomena in mixtures of antioxidants have been investigated and explained. Quantitative criteria have been proposed for the efficiency of inhibition as a function of the structure of the stabilisers (Yu.A.Shlyapnikov, P.I.Levin, E.T.Denisov, V.A.Roginskii, A.F.Lukovnikov, and V.B.Miller).

The mechanism of the photochemical oxidation of solid polymers and the mechanism of the protective action of light stabilisers, which leads (depending on the nature and the type of polymer) to the weakening of the intensity of the incident light as a result of shielding, the quenching of the electronically excited states, the capture of free radicals, and non-radical decomposition of peroxy-compounds, has been investigated (V.Ya.Shlyapintokh and O.N.Karpukhin). The thermal and photochemical reactions of free macroradicals of a series of solid polymers—polycarbonate, poly(methyl methacrylate), polycaproamide, and others—have been studied (D.Ya.Toptygin). The thermal degradation of polymers is being investigated (V.S.Pudov).

The degradation of polymers in liquid and gaseous corrosive media (acids, alkalis, salts, and ozone) has been examined; the chemical degradation processes have been used for the surface modification of polymers. The interaction of polymers with living tissues has been investigated and methods have been devised for the prediction of the stability of polymeric implants (G.E.Zaikov, Yu.V.Moiseev, and S.B.Razumovskii).

A method for the stabilisation of thermostable polymers by introducing into the latter finely dispersed metals formed on decomposition of their organic compounds directly in the polymer has been proposed (G.P.Gladyshev).

The chemistry of sterically hindered phenols has been widely studied and multipurpose antioxidants have been prepared, including stabilisers which are non-toxic and do not colour the polymer. The technology of the manufacture of a series of new stabilisers of the phenolic type, protecting the polymer against thermo-oxidative degradation, has been put forward and developed (A.G.Liakumovich, V.V.Ershov, G.A.Nikiforov, and A.A.Volod'kin).

A new approach to the stabilisation of polymers, based on the specific alteration of their structure by orientational stretching, has been developed (M.Ya.Rapoport).

Studies on the problems of the ageing of stabilisation of polymers are being carried on at Kazan (P.A.Kirpichnikov), Gorky (G.A.Razuvaev and B.B.Troitskii), Tambov (B.N.Gorbunov), Ufa (K.S.Minsker), Leningrad (S.S.Ivanchev and L.I.Lugova), and Moscow (V.V.Korshak, S.V.Vinogradova, S.A.Pavlova, A.B.Blyumenfel'd, and V.V.Gur'yanova).

The mechanism of the action of tribopolymer-forming additives to lubricating-cooling liquids under the conditions of the treatment of metals by cutting has been established; it

is based on the interaction with the metal of the products of the thermomechanical degradation of the additives in the cutting zone (S.G.Entelis and N.V.Kumpanenko).

Studies in the field of polymers with a conjugation system have greatly developed (A.A.Berlin, B.A.Krentsel', and B.E.Davydov). The specific features of the establishment of the supermolecular organisation and properties of these polymers have been discovered and the presence in them of low-lying triplet levels and paramagnetic centres, influencing their reactivity and electrophysical properties, has been demonstrated. The practical importance of the study of the above polymers is associated with their use as photosensitive materials, organic semiconductors, inhibitors of the high-temperature degradation of elastomers and rigid-chain polymers, structure-modifying agents, and a basis for the preparation of plastics with a high thermal stability (A.A.Berlin, B.A.Krentsel', B.E.Davydov, A.A.Ovchinnikov, and L.A.Blyumenfel'd).

Promising studies are being carried out in the field of the formation of polymer-metallic complexes, which are used in catalysis, medicine, and agriculture (S.Sh.Rashidova).

Rapid progress in modern engineering requires the synthesis of polymeric materials with a set of technical properties ensuring their employment over a wide temperature range. Efforts in the synthesis of thermostable polymers have been directed to the preparation of linear chain polymers in which some of the "organic" atoms (hydrogen and carbon) have been replaced by "inorganic" atoms (Si, Al, and Ti).

Among the reactions constituting the basis of the synthesis of polymers with inorganic chains, those involving the polymerisation of inorganic cyclic compounds surrounded by organic groups are of greatest importance. K.A.Andrianov found convenient methods for the synthesis of orthosilicic acid esters and was the first to obtain polyorganosiloxanes, which have found extensive applications in the manufacture of thermostable polymers employed for the thermal and electrical insulation of various articles and for the manufacture of lubricating materials, plastics, rubbers, and paint and varnish coatings. This field of study is being successfully developed (A.A.Zhdanov and S.V.Sokolov).

The studies of N.S.Nametkin have led to the creation of a new class of polymers—polysilico-olefins, which exhibit gas-selective permeability. These polymers are used as highly effective gas-separation membranes, particularly for diffusion-type medical devices which enrich air in oxygen.

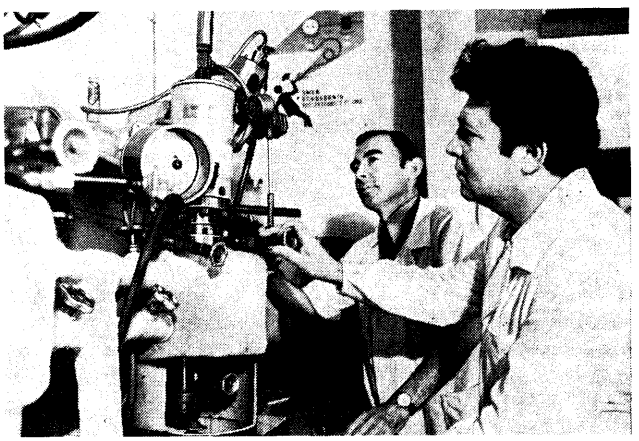


Figure 34. The synthesis of monomers in the Laboratory of Polymerisation Processes of the Institute of the Chemistry and Physics of Polymers of the Academy of Sciences of the Uzbek SSR.

Polymeric materials based on phosphorus-containing compounds (A.E.Arbuzov, B.A.Arbuzov, M.I.Kabachnik, and A.N.Pudovik) and various organoelemental compounds (A.N.Nesmeyanov) have been obtained.

Major advances have been achieved in the synthesis of fluorine-containing polymers (I.L.Knunyants). Approximately 40 types of fluorine-containing plastics, thermostable

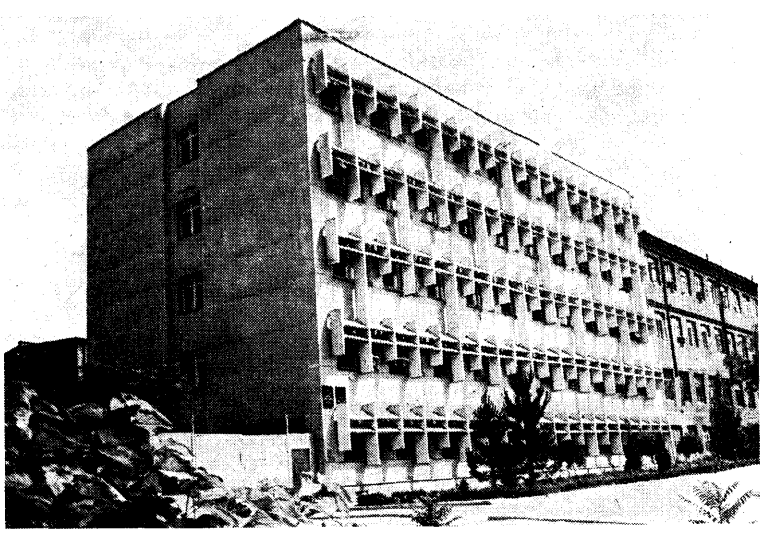


Figure 33. Institute of the Chemistry and Physics of Polymers of the Academy of Sciences of the Uzbek SSR.

fluororubbers with very low glass points, and fluorine-containing oils, which are widely used, particularly in the watch industry, have been synthesised. Perfluoropolymers, with sulpho- or carboxy-groups in the side chains, have been obtained and have been used to prepare membranes which trap mercury in electrolysers for the manufacture of chlorine and caustic alkali. It was observed that among heterochain perfluoropolymers there are some with ultraflexible chains, which is important for the specific synthesis of fluoropolymers with the required properties (V.A.Ponomarenko).

Sulphur-containing polymers of butadiene and isoprene as well as their copolymers with olefins containing bound sulphur in the form of –S–S units, which constitute the basis of materials used in hermetic seals, have been synthesised. In recent years methods have been developed at the Urals Scientific Centre of the USSR Academy of Sciences for the synthesis of titanium-containing oligomers with different structures; cross-linked polymers with a high thermal stability and effective dielectric and adhesion properties have been obtained on their basis. These have been used to manufacture vacuum-tight adhesives and adhesives for ferrite-sital materials.

A.P.Aleksandrov, P.P.Kobeko, and Yu.S.Lazurkin, who were the first to formulate the kinetic concept of relaxation transitions in polymers as a variety of amorphous bodies, have carried out fundamental researches into the physical properties of polymers. This concept was developed further by V.A.Kargin and his school in the form of a system of ideas postulating three physical states of amorphous polymers. Further investigations of the relation between the physicochemical properties of polymers and their structure at the macromolecular level, carried out by this school (N.F.Bakeev, P.V.Kozlov, G.L.Slonimskii, and T.I.Sogolova), led to a theoretical basis for the structural mechanics of polymeric materials and the creation of the foundations of the structural modification of such materials.

At the end of the 1930's the fundamental fact of the thermodynamic reversibility of polymer solutions was established (V.A.Kargin), which initiated detailed studies of the thermodynamics of polymer–solvent systems (S.P.Papkov and A.A.Tager).

M.V.Vol'kenshtein established a field of the statistical mechanics of macromolecules based on a rotational-isomeric model. This theory makes it possible to calculate the geometrical, optical, and electrical characteristics of macromolecules in solution on the basis of their chemical structure. At the same time, it yielded the first interpretation at the molecular level of highly elastic deformation, which was confirmed experimentally. The rotational-isomeric theory, developed subsequently by T.M.Birshtein, Yu.Ya.Gotlib, and O.B.Ptitsyn, received some recognition and became one of the foundations of the modern physics of macromolecules.

V.N.Tsvetkov developed experimental approaches and methods for the determination of the conformations of individual macromolecules in dilute solutions, involving the measurement of streaming birefringence, which have since become classical.

Subsequent theories were characterised by an intense penetration of methods of theoretical physics into the theory of polymers. I.M.Lifshits, A.Yu.Grosberg, and A.R.Khokhlov developed new ideas in the theory of polymer solutions based on the application to the latter of the hypothesis of thermodynamic similarity (scaling). The principal types of phase transitions (coil–globule, liquid crystal ordering, and various versions of phase separation into layers) were investigated. The ideas of theoretical physics have proved extremely fruitful also in the study of the fundamental properties of biological macromolecules.

The research into the liquid crystal state of solutions of rigid-chain polymers were important for the creation of special highly stable high-modulus fibres (S.P.Papkov and S.Ya.Frenkel').

As a result of theoretical and experimental studies, industrial processes were developed for the preparation from flexible-chain polyolefins and polyamides of strengthened filaments with a high degree of polymerisation and strengthened oriented polyethylene films (V.A.Kabanov, N.F.Bakeev, M.M.Koton, and A.S.Chegolya).

Polyolefin fibres with a low degree of polymerisation having the maximum observed (approaching theoretical) moduli of elasticity and strength have been obtained (on the laboratory scale) by orientation with shear under high pressure (N.S.Enikolopov).

Studies in the swelling, plasticisation, and gel formation processes have been carried out in the field of thermodynamics of solutions (A.A.Tager and P.I.Zubov).

Fundamental studies and generalisations in the rheology of polymers have been carried out by P.A.Rebinder and G.V.Vinogradov. Classical investigations of the dielectric properties of polymers were performed (G.P.Mikhailov).

Dielectric spectrometry is at present finding practical applications as a method for the investigation of the processes involved in the formation of three-dimensional structures in polymeric materials during hardening and plasticisation (B.P.Zhukov and N.A.Krivosheev).

Theoretical ideas concerning the nature of the deformation and strength of polymers and reinforced plastics have been developed and the relaxation properties of highly elastic polymers have been studied (A.N.Zhurkov, G.M.Bartenev, V.E.Gul', A.L.Rabinovich, and Yu.M.Malinskii).

A statistical theory of the reactivity of the units of macromolecules has been developed (N.A.Plate and A.P.Litmanovich). The discovery of the phenomenon of microphase separation in graft and block copolymers has played a significant role in the development of methods for the structural-chemical modification of polymers (V.A.Kargin and N.A.Plate).

The problems of the physical chemistry of surface phenomena in polymeric systems have been investigated by Yu.S.Lipatov and Yu.A.El'tekov and the foundations of a theory of adhesion were laid by the researches of B.V.Deryagin, V.E.Basin, and S.S.Voyutskii. The above studies are not only of great theoretical but also of practical importance, particularly for the specific synthesis of adhesives, protective coatings, binders, reinforced plastics, etc. At the present time studies on this problem are directed towards the creation of new types of binders for composite polymeric materials, including "a new generation" of binders which are themselves composite polymeric materials.

Studies on the formation of composite materials based on mixtures of two polymers led to the discovery of the phenomenon of the induced emulsification of one polymer in another, which occurs as a result of thermal and mechanical influences; methods have been developed for the considerable improvement of the mechanical characteristics of polymers produced on a large scale by introducing into the latter small amounts of another polymer (Yu.S.Lipatov and L.M.Sergeeva).

In recent years fundamental studies were directed towards the improvement and development of new processes for the synthesis of polymers and the creation of polymeric and composite materials satisfying the requirements of modern engineering.

An effective procedure for improving the properties of composite materials consisting of elastomers and the articles based on them, which consists in the chemical modification of synthetic raw rubbers both in the manufacturing and processing stages, has been discovered (V.F.Evstratov).

A new promising scientific field—the creation of highly filled polymeric materials by the introduction of mineral and general inorganic fillers directly in the course of the polymerisation of liquid and gaseous monomers—has been developing successfully under the supervision of N.S.Enikolopov.

A fundamentally new method for the preparation of composite polymeric materials, based on the orientational extrusion of polymers in adsorption-active media, has been discovered (M.F.Bakeev and A.L.Volynskii). A new industrial technology for the dyeing of fibres, for rendering them incombustible, and for imparting to them antistatic and bactericidal properties has been developed on the basis of this procedure.

A new general method of synthesis of heterocyclic polybenzazoles involving reductive polyheterocyclisation, which permits the employment of *o*,*o*-dinitrosubstituted nucleophiles as monomers, has been devised (V.V.Korshak and A.L.Rusanov).

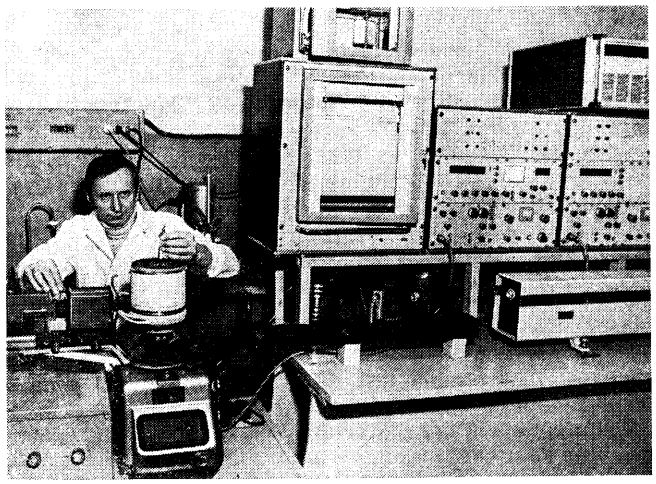


Figure 35. The laser diffractometer for the investigation of the spinodal mechanism of phase separation in binary polymer compositions (Institute of the Chemistry of Macromolecular Compounds of the Academy of Sciences of the Ukrainian SSR).

Studies in the field of anionic polymerisation made it possible to establish a continuous technology for the synthesis of impact-resistant polystyrene. The application of this technology to the stage involving the synthesis of star-like block copolymers, previously obtained only by a periodic method, led to a sharp expansion of the molecular weight and composition distribution (B.A.Dolgoplosk, A.N.Pravednikov, and D.K.Polyakov).

A method of synthesis of thermostable soluble polyamidoimides based on aromatic diamines and imidodicarboxylic acids has been developed. Strong elastic films, used as protective layers in optoelectronic memory devices, flexible foil dielectrics, and protective compounds, have been obtained (M.M.Koton). Research into the preparation of composite materials based on elastomers and of articles directly from oligomeric systems by liquid-phase moulding procedures has been expanded. These studies lead to the possibility of creating more regular vulcanisation networks with the consequent attainment of better technical properties of finished composite materials and articles (V.F.Evstratov).

New methods have been found for the cross-linking of cellulose by solid-phase reactions with bifunctional compounds having hinged linkages and for the cross-linking of cellulose esters via unsaturated weakly substituted derivatives employing orientational effects. Strengthened films and fibrous-sheet cellulose materials have been obtained by these methods (G.A.Petropavlovskii).

Methods have been developed for the synthesis of urethane-containing oligomers and the formation on their basis of composite materials, including photohardening compositions for the preparation of varnishes and coatings (Yu.L.Spirin).

New polymers—polyfunctionally-substituted alkadienyl sulphones and polyphenols, capable of forming thin and strong films and used to prepare highly effective positive electronic resistors and photoresistors—have been synthesised at the Institute of Organochlorine Synthesis of the Academy of Sciences of the Azerbaijan SSR (M.M.Guseinov).

Electrically conducting polymeric radical-ion salts have been synthesised and highly conducting soluble film-forming compositions have been obtained, which leads to interesting possibilities for their practical employment in radioelectronics (A.N.Pravednikov).

Thermotropic liquid crystal polymers, characterised by a helical structure of the mesophase in the solid state, has been achieved. Such polymers selectively reflect light in the visible wavelength range at the usual temperatures, which leads to the possibility of their employment in optics. The orientation of liquid crystal comb polymers of the nematic type in an electric field was achieved for the first time. The condition governing the occurrence of this phenomenon is the presence in the molecule of polar groups which ensure a high dielectric constant. Such highly oriented films may be of interest as polymeric polaroids (N.A.Plate and V.P.Shibaev).

Experimental and theoretical studies on cooperative interpolymer reactions led to the formation of a new class of polymeric materials, including non-stoichiometric water-soluble polyelectrolyte complexes (V.A.Kabanov, A.B.Zezin, and I.M.Papisov).

A method has been developed for the preparation of large blocks of optically homogeneous organic glasses filled with metal compounds, which makes it possible to solve the problem of the formation of polymeric materials resistant to light, heat, and radiation and suitable for light filters with a narrow range of transmission, for the preparation of large plastic scintillators, and for photochromic and thermochromic organic glasses (S.R.Rafikov and coworkers).

The synthesis of macromolecules on templates made of synthetic polymers, modelling the template biosynthesis, was first achieved in the USSR (V.A.Kargin, V.A.Kabanov, and O.V.Kargina). Such template synthesis results in the formation in some cases of ordered polymeric complexes made up of cooperatively interacting chains.

The copolymerisation of monomers from mixtures of vapours on polymeric supports can be used for the template synthesis of macromolecules with a specified alternation of structural elements (B.L.Tsetlin).

Certain advances have been made in the field of polymeric materials for medical purposes. Macromolecular antitubercular and antiviral preparations have been synthesised (V.A.Kropachev and U.N.Musaev).

A large group of polymeric biospecific sorbents based on hydrophilic polymers containing immobilised physiologically active substances (peptides, albumin, heparin, fibrinolysin, and cholesterol) have been synthesised and tested. Such hydrogels and macroporous sorbents can be used to produce haemo-compatible polymeric materials and specific sorbents for the purification and isolation of physiologically active substances (N.A.Plate and G.V.Samsonov).

A biologically active modified water-soluble acroleine–acrylic acid copolymer, which is an active prolonged-action blood anticoagulant, has been prepared. A method has been developed for the preparation of polyaminoesters—a new class of water-soluble ionogenic self-decomposing polymeric compounds, exhibiting a physiological activity. The mechanism of the decomposition of these polymers has been determined.

Purine and pyrimidine derivatives of hydroxyethylcellulose, interacting with complementary polynucleotides as well as promising **antiviral** preparations have been synthesised (N.S.Sidorova).

New "segmented" polyurethanes containing dipeptide units in the main polymer chain have been devised. The polymers have satisfactory thromboresistant properties and can be used to make substitutes for internal organs (Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian SSR, Institute of the Chemistry of Macromolecular Compounds (IKhVS) of the Academy of Sciences of the Ukrainian SSR).

Transplants made of polymeric materials which have shown promise in surgical practice and which have been modified by antimicrobial preparations have been obtained (Institute of the Chemistry of Macromolecular Compounds of the Academy of Sciences of the Ukrainian SSR).

V.A.Kabanov, R.V.Petrov, and R.M.Khaitov developed a new principle for the creation of artificial immunogens by the chemical attachment of antigenic determinants and natural antigens to synthetic membrano-active polymers; this method leads to procedures with a sharp enhancement and the phenotype correction of the immune response.

V. INORGANIC CHEMISTRY

Modern inorganic chemistry constitutes the theoretical and experimental basis for the formation of materials with specified properties and the effective utilisation of natural resources required for scientific and technical progress.

Two main branches of inorganic chemistry—the chemistry of simple and coordination compounds and the chemistry of metals and alloys, rare elements, and semiconducting compounds—are vigorously developing in the USSR.

1. The Chemistry of Simple Compounds

N.S.Kurnakov made a large contribution to the development of the chemistry of simple compounds. He extended the concept of the chemical compound and introduced the idea of a chemical individual, constant- and variable-composition phases (daltonides and bertholides), and a genetic relation between them and the possibility of their interconversion; he suggested the construction of phase diagrams.

All the traditional fields of physicochemical analysis, which has become an objective method for the study of many simplest inorganic compounds and complex systems, have rapidly developed (N.P.Radishchev, V.Ya.Anosov, A.G.Bergman, M.I.Ravich, V.A.Nemilov, G.G.Urazov, V.I.Nikolaev, I.N.Lepeshkov, and A.A.Yakovkin). X-Ray diffraction and spectroscopic research methods have thrown much light in the study of berthollide (N.V.Agreev and E.S.Makarov) and hydride (V.I.Mikheeva) phases.

The numerous studies on the synthesis and physicochemical properties of simple and polyhedral alkali and alkaline earth metal and transition metal hydroborates and binary hydrides, the hydrides of intermetallic compounds, and complex metal hydroborates and hydroaluminates and on the employment of hydride compounds as ligands in transition metal complexes are noteworthy (A.F.Zhigach, V.I.Mikheeva, L.I.Zakharkin, T.N.Dymova, K.N.Semenenko, V.V.Volkov, and N.T.Kuznetsov). The chemistry of peroxy-compounds has been developing at a high rate: simple peroxides, superperoxides, ozonides, and peroxohydrates (I.A.Kazarnovskii, G.P.Nikol'skii, I.I.Vol'nov, and S.Z.Makarov).

Beryllium compounds (A.V.Novoselova), the compounds of rare alkali metals and the elements of the titanium, vanadium, and chromium subgroups (V.I.Spitsyn, E.F.Krauze, and L.I.Kashtanov), and the oxidation of phosphorus and the formation of phosphoric acids (S.I.Vol'fkovich and E.V.Britske) have been investigated. Advances have been made in the chemistry of inorganic compounds of fluorine (I.V.Tananaev, N.S.Nikolaev, Yu.A.Buslaev, I.G.Ryss, and A.V.Pankratov), boron (A.V.Nikolaev, B.F.Ormont, V.A.Epel'baum, and M.A.Gurevich), and zirconium, tantalum, and niobium (N.P.Sazhin and K.A.Bol'shakov).

Numerous studies on the chemistry of simple compounds, designed to investigate their structure and properties, to discover their applications, and to create new materials have been carried out in the last decade.

Fundamental researches have been performed on the chemistry of phosphates containing phosphorus in different oxidation states. Tri- and poly-phosphates of lanthanide metals and tantalum phosphates have been isolated and investigated. Single crystals of bismuth ultraphosphate and optically active films on a support of lanthanum ultraphosphate have been obtained. A brightly luminescent acid phosphito-oxalato-uranyl has been synthesised. Double copper and alkali metal pyrophosphates have been investigated and it has been established that in terms of their specific conductances they are ionic semiconductors. A method has been developed for the synthesis of lanthanide metaphosphates which are necessary for the manufacture of phosphate laser glasses. Vanadium phosphates and condensed neodymium phosphates, which have found applications in quantum electronics as materials for semiconducting glasses, have been synthesised (I.V.Tananaev).

Polymeric ammonium, urea, and alkali and alkaline earth metal phosphates and borophosphates have been investigated in order to employ them in practice as fertilisers, catalysts, and binders. Methods have been developed for the synthesis of condensed phosphates and their structure and principle physicochemical properties have been investigated (S.I.Vol'fkovich).

New data have been obtained on salts of familiar acids such as perchloric, iodic, and boric. A series of studies on the thermal decomposition of perchloric acid and its aqueous solutions have been completed and the mechanism of this reaction has been elucidated (G.B.Manelis, Yu.I.Rubtsov, and V.Ya.Rosolovskii). Methods have been developed for the synthesis of non-solvated perchlorates of polyvalent elements (zinc, boron, aluminium, gallium, iron, titanium, and zirconium) in anhydrous perchloric acid (V.Ya.Rosolovskii), of non-solvated aluminium perchlorate from gaseous perchloric acid (O.N.Breusov), and of spectroscopically pure gaseous, liquid, or solid perchloric acid.

New organic **perchlorates**, including urea, thiourea, and urethane perchlorates have been synthesised and investigated. Anhydrous urethane perchlorate is a new ionic perchlorate which is in the liquid state at room temperature. The reactivities of anhydrous perchlorates of light metals and peroxy-compounds have been studied and solid compositions capable of generating oxygen have been devised. Models of oxygen sources, acting in accordance with the principle of the autocatalytic decomposition of perchlorate and solid mixtures, have been created on the basis of cobalt perchlorates.

Methods of synthesis of peroxy-compounds of nitrogen are being sought. An unstable ammonium peroxonitrate—the

first representative of the salts of pernitric acid—has been obtained (V.Ya.Rosolovskii).

Studies are being prosecuted on the halides of various elements. Mass-spectrometric investigations have been made of the interaction of sodium and caesium fluorides with hafnium fluoride. Single crystals of the type of the pentafluorides of zirconium (hafnium) and alkali metals have been investigated by X-ray diffraction (A.V.Novoselova and Yu.M.Korenev).

The crystal and electronic structures of the fluorides of rare and widely dispersed elements (Yu.V.Gagarinskii) and the fluorides of Group I–VI elements have been studied (V.I.Nefedov). A series of investigations on the synthesis and physical chemistry of inorganic fluorides based on noble gas fluorides and various fluoride halide compounds, which are extremely promising high-energy fluorinating agents, have been made at the Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences.

It has been shown that the thermal decomposition of hexafluoronickel(IV) complexes constitutes a preparatively simple method of production of highly pure fluorine.

An effective synthesis of endothermic noble gas fluorides (KrF_2 and XeF_4) has been achieved for the first time with the aid of the high-temperature generation of atomic fluorine in the presence of a catalyst (nickel). A new class of very powerful oxidants have been synthesised: gold pentafluoride AuF_5 and palladium(V) complexes, which are volatile under the usual conditions; their physicochemical properties have been investigated (V.A.Legasov).

A functional relation has been established between the electron work function and the physical properties of Group IV–VI transition metal borides (I.N.Frantsevich). The available data on the thermodynamic characteristics and compositions of the vapours of the carbides of more than 30 elements have been surveyed. A method has been proposed for the estimation of the thermodynamic properties of binary compounds from their physical properties.

A considerable contribution has been made to the chemistry of natural borates—the thermal "borate effect" has been discovered and borates have been studied by X-ray diffraction (A.V.Nikolaev and E.M.Shvarts).

Methods have been developed for the synthesis of many nitrogen derivatives of boron hydrides and their properties have been studied (V.V.Volkov).

One of the developing fields in organic chemistry is that of the chemistry of hydrides—compounds which are used in various branches of engineering (electronics, optics, homogeneous catalysis, and polymer chemistry).

Methods have been developed for the preparation of extremely volatile inorganic hydrides and chlorides and a series of organometallic compounds. Foundations have been laid for the wide-scale employment of these substances in radioelectronics, fibre optics, and superconductor physics. Ultrapure tin and antimony have been obtained by the decomposition of volatile inorganic hydrides (G.G.Devyatykh).

Many new hydride phases have been synthesised from intermetallic compounds of scandium and the lanthanides with Group VI and VIII transition metals. The high catalytic activity of certain phases in the low-temperature multiple bond hydrogenation reactions has been established.

Scandium, vanadium, iron, and chromium hydroborates and tungsten hydrides have been obtained and investigated. A relation has been established between the type of coordination of the BH_4 group and the crystal-chemical characteristics of the central metal atom (K.N.Semenenko).

A method has been developed for the preparation of specially pure tellurium by the decomposition of hydrogen telluride in the liquid phase by ultraviolet light.

Methods have been devised for the low-temperature synthesis of the oxide nitrides, oxide phosphides, and oxide borides of a number of transition metals—titanium, zirconium, and niobium (Yu.A.Buslaev).

The high thermal stability (up to 1700 °C) of molybdenum disilicide has been investigated, which made it possible to suggest its application in the manufacture of heaters for high-temperature furnaces (G.K.Dubinin, A.P.Slobodskii, and T.D.Timofeeva).

Compounds of various classes exhibiting high thermal chemical stabilities and hardness have been obtained by the method of self-propagating high-temperature synthesis. This procedure has been used to obtain Group IV–VIII metal borides (A.G.Merzhanov). The technology of the self-propagating high-temperature synthesis has been incorporated in several industrial undertakings.

The synthesis of a new ultrahard material—the wurtzite-like boron nitride—under the influence of a shockwave has been developed. The hardness of this substance is close to that of diamond (A.N.Dremin and O.N.Breusov).

The optimum conditions for the synthesis of boron nitride and silicon oxide nitride on metallic and ceramic supports under the conditions of a low-temperature plasma have been determined.

An ionic-plasma technology of the deposition of chromium coatings for the protection of niobium alloys has been developed (A.F.Belov).

Fundamental and applied studies on phase equilibria in complex aqueous salt systems and melts have been carried out and physicochemical studies have been made on natural salts of new salt bearing regions discovered in the Southern Priural'e Territory, Central Asia, and the Volga Region together with the development of methods for their combined utilisation (M.S.Kurnakov, V.M.Nikolaev, V.A.Il'inskii, S.Z.Makarov, I.N.Lepeshkov, and A.V.Nikolaev). The studies of P.P.Budnikov have been devoted to the combined utilisation of the mineral resources of the USSR and to the search for new ways of their employment.

Much attention has been devoted to the development of the theoretical postulates of physicochemical analysis, the topology and metrics of a chemical diagram, and the application of mathematical methods and computers in the development of more rational ways of investigating phase equilibria in heterogeneous systems with different parameters in order to achieve the specific synthesis of new substances and to reduce the volume of laborious experimental investigations.

The method of constructing a chemical diagram of the "composition–property" type has been developed further by introducing new parameters characterising the structure and the degree of dispersion of the system ("composition–structure–degree of dispersion–property"). The method of nuclear relaxation has been successfully applied to the study of the structures of aqueous salt systems at the atomic-molecular level (I.N.Lepeshkov, V.I.Posylaiko, A.S.Trunin, and B.D.Stepin).

Phase equilibria at the solution–melt interface have been investigated in aqueous salt systems at elevated temperatures and pressures and new types of solubility diagrams and the unusual properties of solutions have been discussed.

The high solubility of salts which are virtually insoluble under the usual conditions has been demonstrated. The results obtained have been used successfully to seek the optimum conditions for the growing of single crystals, for the isolation and separation of salts from the mineral raw material, for discovering the mineral formation processes in the Earth's core, and for the creation of a theoretical basis for methods of protecting petroleum extraction equipment from damage by salt deposits (I.N.Lepeshkov and A.V.Nikolaev).

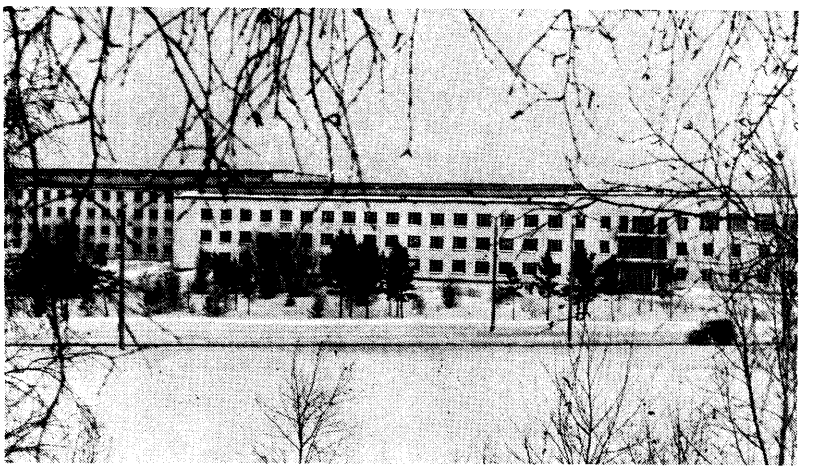


Figure 36. Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences.

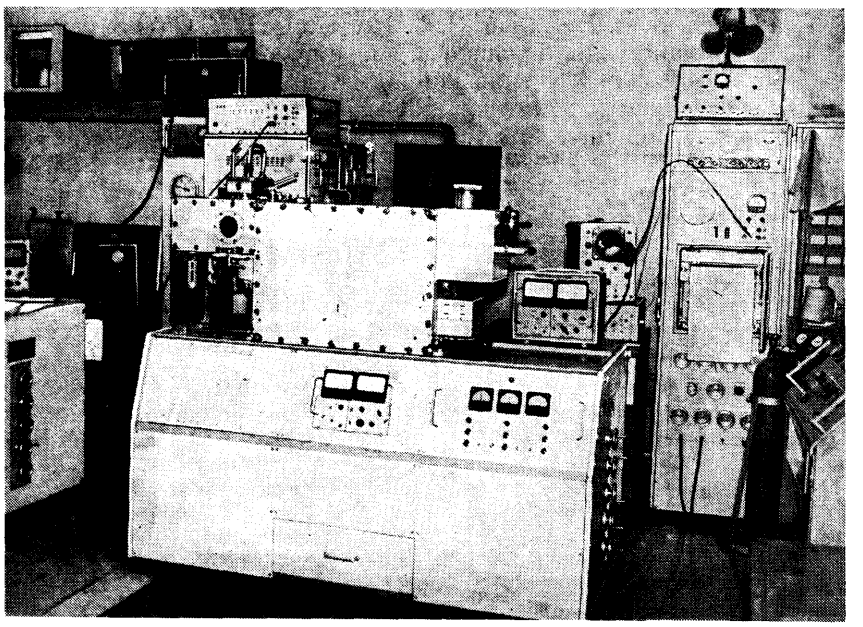


Figure 37. The "Stearat" X-ray spectrometer (Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences).

Extraction methods have been developed for the recovery of boron from the brines in the Volgograd salt-bearing zone and the Kara-Bogaz-Gol and Sivash bays with formation of magnesium chloride brines suitable for the preparation of high-purity magnesium oxide for the requirements of the metallurgical industry and other purposes (I.N.Lepeshkov, D.V.Buinevich, and K.Nogaev).

Inorganic sorbents have been synthesised and the mechanism of the selective action has been investigated, which permitted the solution of a number of problems in the separation of substances, their selective extraction from mixtures, and the preparation of specially pure substances and new materials and carriers for catalysts and also the solution of a number of ecological problems.

Numerous studies have been made on the extraction of nonferrous and noble metals; new selective extractants have been proposed for the extraction of phosphorus and arsenic and for the separation of alkali metals; cation exchangers (based on manganese dioxide and niobium pentoxide) with improved selectivity with respect to sodium and lithium ions have been found; a sorbent for the extraction of boron from natural magnesium chloride brines has been obtained and rational boron extraction methods have been proposed (Yu.A.Zolotov and V.V.Vol'khin).

Methods have been developed for the elimination of nickel impurities from cobalt, for the extraction of copper from concentrated leaching solutions, for the extraction of gold from an antimony electrolyte and a thiocarbamide solution, and for the extraction of platinum metals (I.M.Ivanov, A.N.Khol'kin, and L.M.Gindin).

The extraction of tellurium, tin, and lead by high-molecular-weight amines has been investigated; methods have been proposed for the extraction of boron, lithium, arsenic, and rare metals important for industry from thermal and petroleum waters; a method has been developed for the thorough elimination of molybdenum from tungsten solutions (A.V.Novoselova, V.P.Zlomanov, A.I.Nuriev, and A.N.Zalikman).

The mechanism of the extraction of zirconium fluoride complexes has been investigated (G.A.Yagodin and A.M.Chekmarev).

Extraction-radiochemical and extraction-spectrophotometric methods have been devised for the determination of ultrasmall microamounts of halide ions in the presence of the majority of the elements (cations and anions) of the Periodic System (Yu.A.Baikovskii).

The extraction equilibria involving sulphides and sulphoxides (including their mixtures obtained from petroleum fractions) in relation to aqueous solutions of compounds of nonferrous, rare, and noble metals have been studied.

Study of the heterogeneous equilibria in three-phase systems with layer formation and crystallisation has led to the development of a new method for the separation and purification of substances—the method of extractive crystallisation whereby it is possible to improve greatly the technology of the preparation of specially pure simple inorganic salts (B.D.Stepin).

Modern physical methods and computers are used to determine the structures of inorganic substances.

A system for the input information concerning natural inorganic compounds (minerals) into an automated integral information system for chemistry and chemical technology has been created (G.B.Bokii, N.N.Kochanova, and L.N.Bratchenko).

Methods have been devised whereby it is possible to predict with the aid of a computer the presence in two-component systems of possible inorganic compounds of certain types for 104 known elements of the Periodic System from data for the electronic structures of the atoms of these elements (E.M.Savitskii).

Major advances have been made in the study of X-ray, emission, and absorption spectra of inorganic compounds. A universal combined X-ray spectroscopic apparatus for chemical studies has been constructed. X-Ray spectroscopic studies have been made of the electronic structures of a large number of simple molecules containing nitrogen, sulphur, oxygen, chlorine, carbon, etc. The results of theoretical calculations have been compared directly with the results of experimental studies of the electronic structures of these molecules (L.N.Mazalov).

Information has been obtained about the electronic structures of a large number of inorganic molecules, the ways in which they are coordinated in chemical compounds, the effective atomic charges, the donor–acceptor capacity of ligands and their mutual influence, and surface properties and processes (adsorption, catalysis and corrosion).

2. Metals and Alloys

The most important postulates and characteristics of the formation of alloys and methods for their preparation and for the investigation of their structures and properties under different conditions have been developed by N.S.Kurnakov, A.A.Baikov, P.I.Amosov, L.K.Chernov, and A.A.Bochvar.

The main problems in this field are the elucidation of the nature of interatomic bonds in metals and alloys and the study of the structures and properties of metallic solid solutions and metallic compounds.

N.S.Kurnakov introduced the concept of "solid solutions" and carried out certain generalisations concerning the principles of the continuity of the compositions of metallic phases and the characteristics of the variation of physical properties. Subsequently the application of X-ray diffraction analysis and the development of crystal chemistry led to a revision of the mechanisms of the formation of solid solutions of metals and of the nature of the disposition of atoms at the crystal lattice sites and in the interionic space (N.V.Ageev and G.B.Bokii). G.G.Urazov, N.I.Stepanov, A.T.Grigor'ev, V.A.Nemilov, S.A.Pogodin, and P.Ya.Sal'dau have also been concerned with the study of the physicochemical nature of solid solutions, their structures, and the characteristics of the variation of their properties as a function of composition and with the investigation of systems involving the formation of continuous and organic solid solutions.

In recent years N.V.Ageev, A.A.Bochvar, E.M.Savitskii, N.Kh.Abrikosov, O.S.Ivanov, I.I.Kornikov, V.I.Mikheeva, N.V.Grum-Grzhimailo, and S.I.Gubkin made a large contribution to the theory of phase diagrams and to the development of methods for the investigation of the nature of solid solutions and to the study of the reactions occurring in solid solutions and leading to a change in their physical, mechanical, and other properties.

The phase equilibria in binary, ternary, and a more complex system based on titanium, vanadium, niobium, hafnium, and other metals have been investigated. The changes in the properties of alloys as a function of the phase state have been determined. Studies have been made of a large number of phase diagrams and on the basis of the results new alloy compositions with effective emission, catalytic, magnetic, semiconducting, and other properties have been proposed.

Much attention has been devoted to the problem of the prediction of the phase diagrams for intermetallic compounds (Moscow State University, Institute of Metallurgy of the USSR Academy of Sciences). A method has been developed for the calculation of thermodynamic properties whose results, combined with those obtained with the aid of Wagner's method and the quasi-chemical models of interstitial and substitutional solid solutions, have been used to calculate the phase diagrams for multicomponent metallic systems. A procedure has been proposed for the determination of the phase boundaries in four- and five-component systems using the simplex-lattice design (E.M.Sokolovskaya).

Studies on metallic compounds of various types—metal–metal compounds (two-, three-, and multi-component compounds) and compounds of metals with non-metals (oxygen, hydrogen, nitrogen, silicon, boron, and carbon) yielded new materials with important physicochemical, electrical, magnetic, optical, and mechanical properties.

Especially hard alloys have been synthesised from tungsten, cobalt, titanium, iron, and molybdenum carbides (N.S.Umanskii, G.V.Samsonov, V.N.Eremenko, I.N.Frantsevich, and V.E.Ivanov).

The development of new tungsten-free solid alloys constitutes an important problem. G.B.Shveikin is investigating the synthesis and properties of mixed transition metal (titanium, zirconium, vanadium, niobium, tantalum, etc.) carbide nitrides, oxide nitrides, oxide carbides, oxide borides, etc. As a result of studies of the mechanisms of the interaction of titanium carbide, nitride, and carbide nitride with nickel and molybdenum, a mechanism of the formation of solid alloys based on them has been put forward

and proved. A titanium carbide nitride which can replace the expensive tungsten carbide in soluble alloys has been synthesised and new solid cutting materials have been made from it. The theoretical principles of progressive metallurgical processes and methods of the combined processing of polymetallic ores, whose aim is to create new manufacturing processes for non-ferrous and rare metals, have been developed (A.M.Kunaev).

3. The Chemistry of Rare Elements and Semiconducting Compounds

Rare elements and their compounds are finding extensive applications in various branches of engineering. They are used to prepare protective coatings, high-temperature binders, metal-ceramic articles, heat-resistant glasses and glasses offering protection against radiation, and also as activators in lasers, etc.

Studies in this field were directed mainly to the development of methods for the preparation of high-purity elements and their separation. The development of nuclear power engineering has greatly stimulated the development of the chemistry of rare elements, their separation, and preparation in a pure form.

The development of research in the field of ion exchange, extraction, fine fractionation, and purification by zone melting facilitated the industrial preparation of elements with high and ultrahigh purity. The problem of the separation and preparation in a pure state of zirconium, hafnium, lithium, selenium, and tellurium has been solved.

Extensive studies on compounds of platinoid metals, which constitute the basis for the development of the industrial application of new highly efficient processes for the extraction and refining of precious metals, have been carried out under N.M.Zhavoronkov's supervision.

Extensive investigations have been performed on the synthesis of new laser crystals based on the molybdates and tungstates of the lanthanides and other rare elements (V.I.Spitsyn, L.M.Kovba, V.P.Klevtsov, and M.V.Makhosoev).

In order to find new phosphors and laser materials, studies have been made on the chemistry and thermodynamics of lanthanide and alkali metal phosphates (I.V.Tananaev).

A new class of laser materials—double lanthanide, alkali metal, alkaline earth metal, and transition metal tungstates and molybdates—has been discovered. A technology of the growing of large single crystals of these materials has been developed and applied on an experimental industrial scale, which led to the creation of unique laser devices. Semiconducting elements and compounds occupy a special position in inorganic chemistry. The chemistry of semiconducting compounds is the youngest branch of inorganic chemistry and has developed in the last decades in connection with the requirements of engineering. Methods have been devised for the extensive purification of germanium (N.P.Sazhin, I.P.Alimarin, D.A.Petrov, and I.V.Shmanenkov), silicon (G.G.Devyatykh, B.A.Sakharov, and M.I.Iglitsyn), selenium, and tellurium.

Studies in this field led to the discovery of a large class of binary semiconducting compounds (G.G.Urazov, N.A.Goryunova, A.R.Regel', A.I.Blum, and others). Novel methods have been devised for the synthesis and growing of single crystals of compounds of the types $A^{III}B^{V}$ and $A^{III}B^{VI}$, the chalcogenides of various metals (lead, bismuth, antimony, and others), lanthanide chalcogenides, arsenic sulphides and selenides, and silicon, boron, chromium, rhenium, etc. nitrides, carbides, and silicides (A.V.Novoselova, Yu.I.Gerasimov, I.B.Mizetskaya, L.A.Sysoev, N.Kh.Abrikosov, V.G.Kuznetsov, G.F.Shmelev, B.T.Kolomiets, S.A.Dembovskii, S.V.Nemilov, G.V.Samsonov, V.P.Zhuze, A.A.Eliseeva, and others). Many ternary and more complex semiconducting compounds have been synthesised and investigated.

Studies have been made on ternary compounds in solid solutions based on bismuth selenide (A.V.Novoselova and V.P.Zlomanov), the phase diagrams for systems based on antimony and bismuth halid chalcogenides have been constructed (D.P.Belotskii and N.V.Gavrilenko), and new photosensitive materials based on the chalcogenides of arsenic subgroup elements have been obtained (P.G.Rustamov).

Studies on the synthesis and properties of materials of a new type (ferromagnetic semiconductors based on chalcogen) derivatives of chromium—have been expanded. A number of methods for the synthesis of magnetic semiconductors and for the growing of large single crystals (pure and doped) have been devised. A new field has been established—the chemistry of chalcogenide glass-forming compounds, which made it possible to solve many applied problems (N.M.Zhavoronkov).

The phase diagram for the cadmium–arsenic system has been investigated and the region of its homogeneity has been determined, which made it possible to develop a technology for the preparation of the Cd_5As_2 single crystal with reproducible properties; single crystals of cadmium and zinc phosphides, suitable for the preparation of the resonators in optical quartz lasers with electronic pumping, have been obtained (V.B.Lazarev).

Single crystals of cadmium diarsenide have been prepared and specimens of non-selective detectors of radiant energy have been made from them.

The phase diagrams for the As–S–Se, Ge–As–Te, and As–Te–I systems have been investigated in the glass formation region. The results made it possible to select the optimum compositions of the glasses likely to be suitable for optical instruments, in systems for the recording of images, and in threshold switches and memory cells (S.A.Dembovksii).

The phase diagrams for sulphate, molybdate, and tungstate systems, necessary for the growing of single crystals suitable for practical applications, have been studied.

Inorganic thermostable coatings have been obtained from boron oxides and thin-film condensers have been made in which erbium borate and double lanthanum calcium borate are used as the dielectric layer (B.F.Dzhurinskii).

Many systems involving niobium, tantalum, titanium, lanthanide, and alkali metal oxides have been investigated and the formation of compounds with exceptional electro-optical properties has been established.

The interactions of tungsten and molybdenum oxides with various reductants has been studied under the conditions of a low-temperature plasma and the characteristics of their reduction reactions have been determined (V.P.Elyutin).

Methods have been developed for the first time in world practice for the growing of large single crystals of lanthanide sulphides—materials suitable for the creation of optical and electronic circuits capable of working at elevated temperatures.

Methods of synthesis of stable oxide–crystal structures of indium antimonide, which constitute the basis of integrated photodetectors, have been devised and introduced into practice.

A theory of electroepitaxial deposition has been developed and a new method for the preparation of multilayer modulated structures, used in the design of integrated electronic circuits, has been proposed on its basis and applied in practice.

A technology of the preparation of fibre optics with a quartz glass core doped with germanium dioxide and with a borosilicate coating has been developed. The optical losses

in the fibre optics are determined by the intrinsic scattering in the quartz-germanium glass (G.G.Devyatykh).

The physicochemical principles of the controlled synthesis of semiconducting and ferroelectric materials with specified properties have been determined. The study of "partial component pressure–temperature–composition" diagrams for systems based on the chalcogenides of Group IV elements has been completed. A model has been proposed for the dominant defects in $Pb_{1-x}Sn_xTe$ single crystals and the equilibrium constants for their formation have been determined. The doping of single crystals with indium and gallium in the course of their growth from the vapour has been studied (A.V.Novoselova).

Methods have been devised for the extraction of the raw material for the preparation of rare metals from subterranean thermal and accompanying petroleum waters (V.V.Boldyrev).

4. The Chemistry of Complex Compounds

Traditionally the chemistry of complex compounds is one of the main fields of inorganic chemistry undergoing vigorous development.

The fundamental studies of L.A.Chugaev on the chemistry of platinum compounds led to the synthesis of fundamentally new types of compounds; the structures of complex compounds were determined, studies were made of their interconversions, and the ring rule was established. The studies of I.I.Chernyaev, V.V.Lebedinskii, and A.A.Grinberg also played a major role in the development of the coordination theory of complex compounds.

I.I.Chernyaev formulated the rules governing the *trans*-influence of ligands in complexes. Later B.V.Nekrasov and A.A.Grinberg put forward a physical explanation of the *trans*-influence. Subsequently the stereochemistry of complex compounds was developed on the basis of these rules and the *cis*-influence of ligands was observed.

Many studies have been devoted to the total influence of ligands—the central field in the chemistry of coordination compounds (I.B.Bersuker, A.V.Ablov, K.B.Yatsimirskii, G.M.Shustorovich, and M.A.Porai-Koshits).

I.I.Chernyaev and A.A.Grinberg investigated the mutual influence (*trans*- and *cis*-) of ligands in square planar complexes. Yu.A.Buslaev studied hexacoordination complexes on the basis of the consideration of the electronic structures of compounds containing a multiple covalent metal–ligand bond.

It has been suggested that the ^{19}F chemical shifts in the NMR spectra in mixed fluoride complexes of transition and non-transition elements be used to determine the electron-donating capacity of ligands (E.G.Il'in).

The mutual influence of ligands has been determined by studying the kinetics of the substitution reactions as well as solvation and acid–base equilibria. Compounds with sulphur-containing ligands proved to be satisfactory objects for such investigations (Yu.N.Kukushkin). Instruments permitting the study of complex formation with half-lives down to 10^{-8} s have been constructed and the kinetics of many reactions involving substitution in lanthanide complexes have been studied (K.B.Yatsimirskii and L.I.Budarin).

A thermodynamic scale of the variation of the *trans*-influence has been proposed on the basis of measurements of the p*K* for the acid dissociation of the aquo- and amino-groups in platinum(IV) complexes, which constituted the first attempt at a quantitative characterisation of the *trans*-influence (N.N.Zheligovskaya).

During recent years, studies were made in order to obtain a theoretical explanation of the mutual influence of ligands. The general characteristics of the theory of the mutual influence of ligands in their statistical, kinetics, and thermodynamic aspects and also within the framework of perturbation theory have been examined; direct non-empirical calculations have been made.

A theoretical model of the mutual influence of ligands linked to the central atom mainly by σ-bonds has been developed. The dependence of the mutual σ-influence of ligands on the energy of the valence orbitals of the central atom has been demonstrated and a satisfactory agreement with experimental data has been achieved (Yu.A.Buslaev and V.I.Nefedov).

Many complexes with inorganic and organic ligands have been synthesised. Together with very complex ligands (polyfunctional organic and organoelemental compounds), simple molecules such as N_2, O_2, CO, NO, CO_2, etc. have aroused much interest in recent times; these studies are promising from the standpoint of the solution of many applied problems (the fixation of nitrogen under mild conditions and catalytic processes).

The stereochemical characteristics of the reactions of complexes containing a metal–ligand bond have been determined (Yu.A.Buslaev and Yu.V.Kokunov). Beryllium (A.V.Novoselova and A.I.Grigor'ev) and scandium (L.N.Komissarova and Z.N.Prozorovskaya) have been synthesised in non-aqueous media. Technetium chloride cluster compounds having a fractional degree of oxidation of the metal and incorporating organic and inorganic cations (A.F.Kuzina), platinum and palladium complexes with various ligands (V.I.Spitsyn and N.N.Zheligovskaya), transition metal complexes in non-aqueous media and mixed coordination compounds of titanium(IV) and vandium(IV) with ethanolamine and inorganic acid anions suitable for use in homogeneous catalysis (A.M.Golub), the complexes of many transition, alkali, and alkaline earth metals with macrocyclic ligands containing electron-donating nitrogen, sulphur, and oxygen atoms as well as ether and phosphoryl groups and iron pentacyanide complexes containing molecular nitrogen, the azide ion, nitrous oxide, and other nitrogen-containing ligands (K.B.Yatsimirskii) have been prepared. Organophosphorus complexones permitting the regulation of the calcium metabolism in the organism and exhibiting a high selectivity with respect to lanthanide and transuranic elements (N.M.Dyatlova and V.Ya.Temkina), the coordination compounds of platinum and heavy metals and uranium, and transition metal complexes of various hydrazides (R.N.Shchelokov) have also been obtained.

Studies have been made on the sulphoxide complexes of platinum metals which led to the discovery of the unique properties of dialkyl sulphoxides as ligands (Yu.N.Kukushkin).

The conditions for the synthesis of the coordination compounds of transition metals with polydentate ligands and the mechanisms of ligand substitution reactions in the inner sphere have been studied (A.V.Ablov).

The hitherto unknown lead(II) complexes have been synthesised and investigated and highly effective narrow-band phosphors, transforming both ultraviolet and infrared radiation into visible light, have been developed on their basis.

A photochromic material whereby a multicoloured image can be obtained has been synthesised from molybdenum(VI) complexes with cellulose derivatives and the possibility of its employment in the cartographic industry has been demonstrated.

A large group of compounds of tervalent antimony with six ligands were synthesised for the first time (Yu.V.Gagarinskii).

The study of the coordinating capacity of the perchlorate ion made it possible to devise methods for the synthesis of a new class of inorganic compounds—the complex perchlorates of light elements. It had been believed for a long time

that perchlorates are incapable of complex formation (V.Ya.Rosolovskii).

Methods have been developed for the synthesis of fluorine-containing complexes of noble metals and the phenomenon of the structural non-equivalence of the fluoro-ligands in the structure of the complex anion was demonstrated for the first time (B.I.Peshchevitskii and S.V.Zemskov).

I.V.Tananaev investigated uranium, plutonium, and thorium fluorides and oxide fluorides and the higher fluorides of the elements of the chromium and vanadium subgroups.

A new field of coordination chemistry, namely the chemistry of the complexes of higher sulphoxides, has been developed.

Systematic researches are being prosecuted into macrocyclic ligands, which serve as models of membrano-active complexones; macrocylic ligands of a fundamentally new type—ligands containing the reactive phosphoryl group in the macroring—have been synthesised and studied (K.B.Yatsimirskii).

Many macrocylic organic compounds containing oxygen, nitrogen, and sulphur atoms have been synthesised in order to find reagents selective with respect to individual metal ions. Extractants selective with respect to copper and mercury compounds have been discovered (Yu.A.Zolotov).

Studies on the chemistry of lanthanide complexes have developed on a wide scale. The existence of a new class of lanthanide complexes, characterised by the polarisation and the electrostatic interaction of the central atom with the ligand, in contrast to the complexes of the classical type having distinct homeopolar bonds, has been demonstrated experimentally and justified theoretically.

The dependence of the stability of lanthanide complexes on the atomic number of the element, the acidity of the reaction medium, and the properties of the ligands has been studied (M.M.Senyavin, V.G.Lebedev, and D.I.Ryabchikov).

The complex formation phenomenon constitutes the basis of methods for the separation of the lanthanide elements (liquid–liquid extraction, ion-exchange chromatography, fractional crystallisation, etc.). Systematic studies of lanthanide complexonates by various physicochemical methods made it possible to achieve a theoretical basis for the selection of the optimum conditions for the separation of mixtures of lanthanide elements with the aid of ion-exchange chromatography (V.I.Spitsyn and L.A.Martynenko) and by the extraction method (G.V.Korpusov).

The properties and applications of lanthanide β-diketonates have been studied. The quantitative gas-chromatographic separation of the lanthanide elements with the aid of β-diketonates has been achieved (L.A.Martynenko and N.A.Kostromina).

The complexes of heteropolycompounds have been studied (E.A.Nikitina).

The problem of the basicity of heteropolyacids with non-metal central atoms (phosphorus and silicon) has been solved in relation to molybdophosphoric, tungstophosphoric, molybdosilicic, etc. acids. The nature and characteristics of the chemistry of heteropolymolybdenum compounds of cerium, thorium, uranium(IV), and neptunium(IV), which are distinguished by an unusual coordination of the central atom and a high basicity, have been studied.

Many heteropolycompounds capable of functioning as ligands in relation to alkaline earth, lanthanide, and transuranic metals have been synthesised with the aid of a new method for the isolation of heteropolyacids in a crystalline form; this permitted the synthesis of stable compounds of neptunium(VII) and the development of methods for its analytical determination (V.I.Spitsyn, E.A.Torchenkova, and V.F.Chuvaev).

Advances have been made in the synthesis of new representatives of heteropolycompounds (A.I.Kokorin and A.K.Babko). Methods have been developed for the synthesis of complexes with cyclic polydentate ligands—phosphinates, and the characteristic features of the conformation of the ring in the inner sphere of the complex have been established (I.A.Rozanov).

Various physical and physicochemical methods have been widely used in the investigation of the mechanisms of complex formation reactions and the structure and properties of the complexes.

A series of structural investigations of lanthanide heteroligand complexes, whereby significant differences were established in their tendency towards the formation of bonds between the lanthanide elements and chlorine, thiocyanate and nitrate groups, have been carried out (M.A.Porai-Koshits).

Structural investigations of a series of new palladium complexes established the existence of hitherto unknown types of σ-bonds between palladium and naphthene and quinonoid ligands (L.O.Atovmyan, V.A.Avilov, and O.N.Krasochkina).

The X-ray diffraction method has also been used to elucidate the structure of phenanthrolinium dioxotetrabromouranate (R.N.Shchelokov), for the investigation of the nickel, cobalt, copper, and alkali and transtion metal complexes with macrocyclic ligands (K.B.Yatsimirskii), transition metal complexes with polydentate ligands (A.V.Ablov), tervalent antimony complexes with mixed acido-ligands (Yu.V.Gagarinskii) and the stereochemistry of lanthanide complexes (L.I.Martynenko) and for the elucidation of the structures of new promising biologically important coordination compounds.

The complex formation reactions of paramagnetic ions in solutions have been investigated by EPR (I.N.Marov, A.N.Ermakov, V.K.Belyaeva, and Yu.N.Dubrov).

The complex formation reactions of the lanthanide elements with a number of aminoacids and sulphosalicyclic and diethylmalonic acid in aqueous solutions (N.A.Kostromina), the formation of complexes between vanadium and ascorbic acid (K.B.Yatsimirskii) and between molybdenum and catechol (A.G.Pilipenko), platinum complexes, many lanthanide complexes (V.I.Spitsyn, N.N.Zheligovskaya, L.I.Martynenko, and R.N.Shchelokov), coordination compounds of transition metals with amines, amides, and primary hydrazides, and complexes with biologically active ligands (Yu.Ya.Kharitonov and O.Yu.Tsivadze) have been investigated by polarographic, spectrophotometric, potentiometric, NMR, EPR, ^{1}H NMR, infrared spectroscopic, etc. methods. The kinetics of the formation reactions of cobalt, copper, and cadmium complexes with chlorophyllic acid in non-aqueous solvents have been investigated (B.D.Berezin).

Electrophotometric studies have been carried out to determine the contents of osmium, ruthenium, and a number of other metals in natural and industrial objects (A.I.Busev and V.M.Peshkova).

The magnetochemical method was developed further in the chemistry of coordination compounds (V.V.Zelentsov). The theoretical principles of the interpretation of the magnetic properties of cluster and polynuclear compounds have been deduced, a model explaining the unusual magnetic properties of a new type of iron(III) chelates has been proposed, and the magnetochemical criteria for the assessment of the stereochemistry of cobalt(II) complexes have been analysed (V.V.Zelentsov).

The possibility of employing the spin echo method to investigate transition metal complexes with heterogeneous ligands in the inner sphere has been demonstrated (A.A.Popel').

Mathematical modelling has been used to investigate complex formation in systems containing mixed-ligand lanthanide complexes (L.I.Martynenko).

5. Radiochemistry

Among the first investigators of this new field of chemistry, mention should be made of V.I.Vernadskii, V.G.Khlopin, V.A.Borodovskii, G.N.Antonov, Vl.I.Spitsyn, L.S.Kolovrat-Chervinskii, A.P.Sokolov, and E.S.Burkser, who carried out extensive studies on the radioactivities of natural objects on Russion territory and of the physicochemical properties of natural radioactive elements.

The founder, organiser, and inspirer of the planned investigation of radioactive minerals and the search for them on Russian territory was V.I.Vernadskii.

V.G.Khlopin, who supervised since 1918 all the research in our country on the isolation of natural radioactive elements and the study of their physicochemical properties, is regarded as the founder of Soviet radiochemistry. He proposed a method whereby highly active radium preparations can be obtained, which was used subsequently in the first radium factory in Soviet Russia for the extraction of this element from USSR ore. During subsequent years studies were carried out jointly with B.A.Nikitin, A.E.Polesitskii, A.P.Ratner, and I.E.Starik on the distribution of radioactive elements between the crystalline solid phase and the solution. These investigations showed that the characteristics of the distribution of radioactive elements between different phases are determined exclusively by their chemical state and are independent of the concentration (when the phases are saturated), be they trace concentrations or macroconcentrations (Khlopin's Law).

The results of these studies served as the basis for an enormous number of methods for the investigation, purification, isolation, and concentration of radioactive elements and became the theoretical foundation on which Soviet radiochemistry developed during the subsequent decades.

Since the beginning of the 1930's, the number of realised nuclear reactions has been increasing and there has been a corresponding increase in the need to identify and investigate the chemical nature of the products of these reactions with the subsequent possibility of their isolation in large amounts.

In connection with the discovery of nuclear fission (G.N.Flerov and K.A.Peterzhak), the centre of gravity of radiochemical research shifted to the study of the chemistry of thorium and uranium. Soviet radiochemists (B.A.Nikitin, V.M.Vdovenko, M.F.Pushlenkov, and V.B.Shevchenko) begun to investigate the distribution of uranium nitrates and then plutonium and neptunium nitrates between two liquid phases—aqueous and organic, which made it possible subsequently to devise extraction schemes for the processing of irradiated uranium using various organic solvents as extractants (tributyl phosphate, aliphatic amines, etc.).

Later extraction methods were used to separate the lanthanide elements from one another and from transplutonic elements and to obtain radionuclides without carriers (N.E.Brezhneva, An.S.Nesmeyanov, and A.K.Lavrukhina).

The researches of V.M.Vdovenko, M.F.Pushlenkov, V.V.Fomin, A.V.Nikolaev, G.A.Yagodin, V.S.Shmidt, A.M.Rozen, Yu.A.Zolotov, V.S.Koltunov, and S.M.Karpacheva involved the study of mechanisms and kinetics of extraction processes and of the influence of various factors on them, such as the composition and structure of the aqueous phase, the oxidation-reduction reactions occurring in the extraction process, the complex formation reactions of the extracted elements in the organic phase, and the structure of organic extractants.

Many preparative and technological tasks (the preparation of radionuclides without carriers, the separation of radionuclides, and their concentration) are being solved by the ion exchange method.

B.P.Nikol'skii, B.N.Laskorin, V.I.Paramonova, and B.A.Zaitsev determined the fundamental characteristics of the sorption of radioactive elements by various adsorbents (glass, crystals, synthetic resins, and inorganic sorbents) and elucidated the influence of various factors on this process.

The development of atomic power engineering, which was initiated in 1954 by the start of the operation of the first atomic electric power station in the Soviet Union, gave rise to new important problems in radiochemistry and radiochemical technology. One of the most important fields of applied radiochemistry involves the development of the theoretical principles of the technology of the processing of irradiated fuel from atomic power stations in order to devise economical methods for the extraction and the return to the fuel cycle of valuable components and, in the first place, fissionable materials.

The development of atomic power engineering, the growth of the mining industry, and the wide-scale application of radionuclides in the national economy increased the potential risk of contamination of the environment, particularly the biosphere, by radioactive substances. The problem of rendering harmless radioactive waste containing long-lived isotopes and their reliable isolation is most important at the present time.

I.V.Petryanov-Sokolov, V.I.Spitsyn, A.S.Nikiforov, N.E.Brezhneva, B.S.Kolychev, I.E.Nakhutin, N.V.Zimakov, V.V.Kulichenko, V.M.Sedov, and A.A.Konstantinovich have made a great contribution to the creation of methods whereby radioactive isotopes (solid, liquid, and gaseous) have been made harmless and stored.

The most important field of radiochemistry is radiochemical analysis in which cocrystallisations, sorption, extraction, the electrochemical isolation method, etc. are used. The foundations of radiochemical analysis were laid in the studies by V.G.Khlopin, A.E.Polesitskii, I.E.Starik, P.N.Palei, and especially A.P.Vinogradov.

A number of problems concerning the degree of control of nuclear materials, the degree of utilisation of nuclear fuel, the exact determination of the content of fissionable materials, and the determination of their active composition have now been solved as a result of the studies of I.P.Alimarin, B.F.Myasoedov, A.A.Lipovskii, V.K.Markov, and I.K.Shvetsov.

Much attention is devoted by Soviet radiochemists to the monitoring of the territorial and temporal distribution of technogenic radionuclides on the Earths surface, water reservoirs, soils, and objects in living nature (V.I.Spitsyn, An.N.Nesmeyanov, P.K.Khabibullaev, A.A.Kist, V.P.Shvedov, Yu.V.Kuznetsov, D.I.Gusev, E.N.Teverovskii, and L.I.Gedeonov). Various methods have been developed for the determination of low and vanishingly low concentrations of radioactive substances in objects in the environment.

The fundamental researches by Soviet scientists into the chemical and physical properties of natural and artificial radioactive elements must be regarded as the most important achievements in radiochemistry.

The studies of V.G.Khlopin, B.A.Nikitin, B.P.Nikol'skii, and Z.V.Ershova on the chemistry of radium, radon, and polonium were in many respects fundamental.

The studies of I.I.Chernyaev, A.A.Grinberg, V.I.Spitsyn, A.D.Gel'man, V.D.Nikol'skii, A.I.Vol'skii, V.M.Vdovenko, N.P.Zefirov, A.S.Nikiforov, and L.P.Sokhina on the chemistry of thorium, uranium, neptunium, plutonium, and certain other radioactive elements made a significant contribution to the knowledge of many rules governing their physicochemical properties and behaviour under various conditions and also permitted the solution of a number of major practical problems.

Extensive studies are being prosecuted at the present time on the chemistry of radioactive elements. Heptavalent neptunium and americium, hexavalent californium, bivalent fermium and einsteinium, and univalent mendelevium were obtained for the first time ever. The principles of the coordination chemistry of actinoyl ions (AnO_2^+) were determined. A method was devised for the stabilisation of transplutonium elements in solutions in the quadrivalent state, which is of great practical importance (V.I.Spitsyn, G.P.Yakovlev, N.N.Krot, A.G.Rykov, V.S.Shmidt, L.N.Lazarev, D.N.Suglobov, N.B.Mikheev, and V.N.Kosyakov). A whole series of hitherto unknown technetium compounds were synthesised and their physicochemical properties investigated (V.I.Spitsyn and A.F.Kuzina).

Significant advances have been made in the synthesis and the study of the chemical properties of superheavy elements. After the synthesis of kurchatovium, Soviet chemists obtained for the first time, under G.N.Felerov's supervision, elements with atomic numbers of 105, 106, and 107. The first reliable results confirming the possibility of the existence of superheavy elements in nature were obtained.

The manufacture of isotopes was organised in the USSR more than 30 years ago. Isotopes, labelled compounds, and sources of nuclear radiation are being produced at the present time in amounts satisfying the requirements of the national economy. Almost all the radioactive and stable isotopes of practical importance are being produced. A whole series of labelled compounds, including biologically active compounds (aminoacids, nucleotides, and steroids), plant protecting agents (herbicides, insectofungicides, and growth initiators), and preparations for diagnostics and therapy are being manufactured.

A.S.Nikiforov, V.V.Bochkarev, N.E.Brezhneva, D.M.Ziv, I.F.Tupitsyn, and G.S.Sinitsyna have made a large contribution to the development of these researches and the initiation of the industrial production of isotopes in the USSR.

VI. ANALYTICAL CHEMISTRY

The present state of analytical chemistry is characterised by major advances in the development of fundamental theoretical principles, the successful development of various highly efficient analytical methods, and the enormous contribution that analytical chemistry has made and continues to make to the solution of the most important scientific and technical problems of the modern age (the mastering of the energy of the atomic nucleus, the study of space and the ocean, the development of electronics, and progress in biological sciences). The growth of analytical chemistry made it possible to monitor many modern technological processes and the quality of current production in the chemical, metallurgical, pharmaceutical and food industries and also the purity of the environment—water, air, and soil. Soviet analytical chemistry occupies a leading position in the world in many fields such as analysis of highly pure substances, analysis of minerals, studies on organic and analytical reagents, and photometry.

The scientific establishments of the USSR Academy of Sciences and the Academies of Sciences of the Union Republics as well as Branch Institutes have played an enormous role in the laying of the foundations and the development of methods of analytical chemistry.

Among the latest advances in analytical chemistry, mention should be made in the first place of the remote elemental analysis of the soil on the planet Venus, thorough analytical study of the lunar soil, and the development of a set of analytical methods and instruments for the analysis of specially pure substances. Studies designed to devise methods and detecting systems for the analytical monitoring of the manufacture of ultrapure organic substances and biological materials, including those obtained in space, have now been expanded over a wide front.

Analytical chemistry has developed in close association with the growing needs of the national economy.

During the first years of the socialist construction in the USSR, major researches into the analytical chemistry of platinum metals and their compounds and the application of complexes in analytical chemistry were performed under the supervision of L.A.Chugaev, N.S.Kurnakov, V.V.Lebedinskii, N.I.Podkopaev, V.G.Khlopin, B.G.Karpov, I.I.Chernyaev, and O.E.Zvyagintsev. The studies of V.I.Vernadskii, V.G.Khlopin, K.A.Nenadkevich, and I.D.Borneman-Starynkevich have been important in the analysis of minerals and in the solution of problems associated with the development of chemical and physical methods for the monitoring of the production of radium, uranium, and vanadium.

In the 1930's–1950's the development of large-scale and rapid monitoring methods promoted the development of the rare metals industry and a number of new chemical manufacturing processes. Fundamental studies were carried out on the physicochemical analysis of systems important for analytical chemistry (I.V.Tananaev and A.K.Babko) and the kinetic analytical methods (K.B.Yatsimirskii). Together with the development and improvement of classical methods of analysis—gravimetric (N.A.Tananaev) and titrimetric (V.S.Syrokomskii and R.P.Lastovskii)—physicochemical and in the first place electrochemical analytical methods began to be widely used and have still not lost their importance. The introduction of polarography in our country is associated with the names of V.I.Vernadskii and A.P.Vinogradov. The fundamental researches by the largest school of electrochemists founded by A.N.Frumkin were very important for the development of this method. Coulometry (M.T.Kozlovskii) and other electro-analytical methods (B.N.Nikol'skii, Yu.S.Lyalikov, and O.A.Songin) have been developing successfully.

Notable advances have been made in devising direct potentiometric analytical methods using ion-selective electrodes for different purposes, for example, for the determination of hydrogen, fluoride, chloride, and sulphate ions. The studies by B.P.Nikol'skii and M.M.Shul'ts on the theory and practice of potentiometric pH titrations were important in this field.

Photometric analytical methods and the determination of their physicochemical principles have developed vigorously. Numerous photometric methods for the analysis of metals, alloys, and minerals were devised. Many analytical organic reagents suitable for the qualitative and quantitative determination of almost all the elements have been synthesised and applied in practice (A.S.Komarovskii, L.M.Kul'berg, V.I.Kuznetsov, S.B.Savvin, A.M.Lukin, A.T.Pilipenko, N.S.Poluektov, Yu.A.Bankovskii, and V.M.Tarayan).

Among the reagents proposed by Soviet scientists, special mention should be made of Arsenazo III (S.B.Savvin), which is widely used in world practice, and is an excellent reagent for the photometric determination of uranium, thorium, plutonium, zirconium, and many other metals in objects of a wide variety of kinds. The successful development of a theory of luminescence methods and their practical employment is associated with the work of S.I.Vavilov, M.A.Konstantinova-Shlezinger, E.A.Bozhevol'nov, N.S.Poluektov, A.K.Babko, A.T.Pilipenko, and D.T.Shcherbov.

Spectroscopic analysis became one of the most important analytical monitoring methods in industry and scientific laboratories. Considerable progress in studies on emission spectroscopic analysis and also luminescence and emission flame photometric methods was based on studies of

G.S.Landsberg and L.I.Mandel'shtam. The possibilities of the atomic-emission analytical method have greatly expanded at the present time with the appearance of new spectral excitation sources, particularly inductively bound plasma, which permits the simultaneous determination of 60–70 elements with a high sensitivity and accuracy.

One of the particularly important problems, namely that of the unification of analytical methods for metals, was solved (A.M.Dymov) and served as a basis for the creation of the first USSR Government Standards (GOST) for the industrial production and led to a large series of studies on the standardisation of analytical methods in the USSR and later within the framework of the countries of the Socialist Economic Community (SEV).

The extensive employment in various branches of the national economy (metallurgy, atomic power engineering, and radioelectronics) of many rare and scarce elements and a stringent requirement for their purities stimulated a considerable development of studies on the theoretical problems of the analytical chemistry of these elements and the development of new methods for their separation and determination. A.P.Vinogradov, I.P.Alimarin, I.V.Tananaev, D.I.Ryabchikov, N.S.Poluektov, V.A.Nazarenko, and Yu.A.Chernikhov made a considerable contribution to the growth of this branch of analytical chemistry.

The analytical chemistry of uranium, plutonium, and transplutonium elements has developed successfully (A.P.Vinogradov, P.N.Palei, B.F.Myasoedov). During the current five year plan, the publication of a fundamental series of monographs on "The Analytical Chemistry of the Elements" (approximately 60 volumes) is being completed.

During the 1960's–1970's, when problems of a sharp increase in the sensitivity of analytical methods arose in connection with the need to analyse atomic materials, semiconductors, and other highly pure substances, radioactivation analysis and spark mass spectrometry as well as chemical spectroscopic, voltamperometric, and other methods were developed, whereby down to 10^{-6}–10^{-8}% of impurities can be determined in pure substances. The introduction of highly sensitive reliable analytical methods made it possible to solve the most important problem of the national economy, namely to ensure the development of branches of the new technology such as instrument making, radioengineering, atomic power engineering, high pressure techniques, and the manufacture of specially pure substances and reagents (I.P.Alimarin, N.P.Sazhin, Yu.A.Zolotov, G.G.Devyatykh, Yu.A.Karpov, Yu.V.Yakovlev, and M.S.Chupakhin).

The enormous scale of the industrial manufacture of organic compounds stimulated the development of theories and new methods of analysis of organic compounds. Important studies have been carried out on the elemental and functional analysis of organic substances and its automation (A.P.Terent'ev, M.O.Korshun, and V.A.Klimova). Infrared spectroscopy and electrochemical, chormatographic, and chromatomass-spectrometric methods are widely employed.

The atomic absorption analytical method is being improved in order to make it a multielement method. The non-flame versions of the method, particularly those employing a graphite furnace as the atomiser, are being vigorously developed (B.V.L'vov).

Among the X-ray analytical methods one of the most important (and among analytical methods in general) places has been taken by X-ray fluorescence analysis, which makes it possible to determine simultaneously almost all the elements (with the exception of the lightest) in the concentration range from 10^{-4} to 100% with an extremely high accuracy. The rapidity and high productivity of the method permit the solution with its aid of the problems of high-speed analysis in metallurgy and in the geological service (A.P.Nikol'skii, M.A.Blokhin, N.F.Losev, and V.P.Afonin). The X-ray spectroscopic microanalysis (the electron prove method) (I.V.Borovskii and N.P.Il'in), whose maximum sensitivity is 10^{-13}–10^{-15} g, permits a reliable investigation of various inclusions in metals, alloys, and geological specimens, deposits, etc. X-Ray electronic spectroscopy proved to be extremely promising in the study of the compositions of surface layers and films (V.I.Nefedov).

The analytical scope of the EPR method has greatly expanded in connection with the employment of complex-forming reagents based on stable free radicals (P.M.Solozhenkin, I.N.Marov, and Yu.A.Zolotov).

A completely new procedure in laser spectroscopy is being developed, namely the method of stepwise photoionisation of atoms (V.S.Letokhov and Yu.Ya.Kuzyakhov), which can be absolutely selective and has a maximal sensitivity, since it permits the determination of impurities amounting to tens and even several atoms.

The researches into the theory and practical applications of chromatographic separation methods using ion-exchange resins and inorganic and chelate sorbents have undergone an extensive development (K.V.Chmutov and M.M.Senyavin).

Numerous procedures have been devised for the separation of complex mixtures in the analysis of semiconducting materials, noble and non-ferrous metals, their alloys, and materials required for the atomic industry, minerals, and other objects. Thin-layer and paper chromatography have come to be widely used, particularly in organic analysis.

There has been rapid progress in high-speed liquid chromatography under pressure. The new method of ionic chromatography has been devised and is being developed (Yu.A.Zolotov). It is the automated high-speed version of ion-exchange chromatography.

A new chromatographic method—gel permeation chromatography—which is important for the separation of natural and other organic substances, has been widely employed in recent years.

Extraction has become one of the commonest methods for the separation and concentration of substances. I.P.Alimarin, V.I.Kuznetsov, and Yu.A.Zolotov, who specialise in radiochemistry, and A.T.Pilipenko and Yu.A.Bankovskii made a significant contribution to the theory of extraction processes, the synthesis and study of new reagents, and the development of effective extraction methods and their application to analytical chemistry. Studies in fields at the boundary between extraction and chromatography, particularly on extraction, chromatography (I.P.Alimarin and G.S.Katykhin) and the introduction of selective sorbents (Yu.A.Zolotov and S.B.Savvin), are of great importance. In particular, procedures have been developed for the separation of mixtures of the lanthanide and actinide elements and methods for the concentration of various microelements.

Different versions of radioactivation analysis are developing vigorously—activation by slow, resonance, and fast neutrons, gamma-quanta, and charged particles. In combination with the new methods for the concentration and isolation of elements (extraction, extraction chromatography, coprecipitation, and ion exchange), the above procedure has become extremely common in the analysis of semiconductors, specially pure substances, metals, alloys, geological and biological objects, objects in the environment, etc. (I.P.Alimarin, Yu.V.Yakovlev, A.A.Kist, and E.M.Lobanov). A significant expansion of the applications of the above method has been achieved as a result of the employment of portable neutron sources (californium-252).

The creation of the Soviet manufacture of analytical instruments has in many respects promoted the successful development of analytical chemistry and the organisation of the

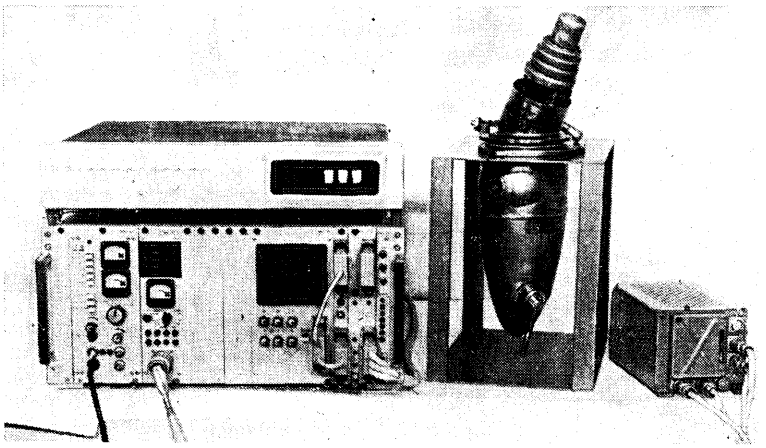


Figure 38. The set of scientific apparatus of the "Venera-13" and "Venera-14" automatic interplanetary stations for the analysis of rocks on the surface of Venus.

effective monitoring of the chemical composition of the products in chemical industry.

The unique set of scientific apparatus for the "Venera-13" and "Venera-14" automatic interplanetary stations, whereby direct sampling and X-ray fluorescence analysis of the rocks on the surface of Venus and the transmission of information to the Earth was achieved, may serve as an example of the possibilities of Soviet instrument making (V.L.Barsukov and Yu.A.Surkov).

An extremely characteristic feature of modern analytical chemistry is the incorporation of mathematical theory and methods, particularly methods employing computers, which play a considerable role in the automation of analysis. The creation of automated analytical instruments and sets with a wide variety of purposes made it possible to achieve a considerable improvement in the analytical monitoring of industrial processes and also in routine determinations in the geological service, in the protection of the environment, in agriculture, and in medicine.

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Soviet chemical science embraces all the principal developments in modern chemistry. In all these developments our chemists have made outstanding and generally recognised contributions to world science.

The 60th anniversary of the foundation of the USSR is celebrated by soviet chemists by new discoveries and achievements to the glory of their great Motherland.