All this puts great responsibility on chemists, who are armed with modern methods of investigation and the resolve to make a worthwhile contribution to the common task of building a communist society.

Extensive development of theoretical research in all areas of chemistry and a strengthening of the links with industry—these are the most important aims put before Soviet scientists by the XXIIIth Congress of the Communist Party of the Soviet Union, goals which will doubtless be achieved. The remarkable achievements of Soviet chemistry during the fifty years of Soviet rule are a guarantee of this.

U.D.C. 546

FIFTY YEARS OF DEVELOPMENT OF INORGANIC CHEMISTRY IN THE SOVIET UNION

V.I.Spitsyn

The Great October Socialist Revolution opened up unprecedented possibilities for the development of science in the Soviet Union. In fifty years, an extensive network of research centres has been created, and large numbers of teams of highly qualified specialists have been educated and trained for these centres. Considerable success has been achieved in the planned development of science and in the coordination of its various branches.

The intensive growth of theoretical and applied studies, together with the general sharp increase in the industrial potential of the country, has created favourable conditions for the development of strong Soviet research schools, many of which have now obtained world recognition.

It was the creation of a strong science-backed industrial basis for the new technology in the Soviet Union that enabled the country to withstand the severe trials of the Great Patriotic War against German fascism. The same factors in the post-war years made it possible in a short time to resolve such complex problems as the creation of an atomic industry and nuclear energy, the construction of powerful rockets and the development of propellants for them, the organisation of the production of semiconductor and laser materials, etc. Here an important part has been played by the chemical sciences, and by inorganic chemistry in particular.

Inorganic chemistry originated in Russia two hundred years ago when M. V. Lomonosov carried out studies of the oxidation of metals, of outstanding scientific importance, and for the first time on the basis of experimental data formulated the law of conservation of matter. In 1869, D. I. Mendeleev made an outstanding contribution to the development of world science by his discovery of the Periodic Law governing the chemical elements; this law represents the greatest generalisation of our knowledge in the field of inorganic chemistry. The Periodic Law formed the basis for the development of subsequent work involving the study of atomic structure, the phenomena of radioactivity, and the synthesis of new chemical elements.

Scientists in Russia developed the theory of solutions and carried out studies of the platinum metals, one result of which was the discovery of the element ruthenium. Silicates, peroxides, salt ammines, crystal hydrates, and the radioactive elements were studied. The foundations were laid for the development of the method of physicochemical analysis, which has given particularly valuable results in the study of alloys and intermetallic compounds.

Despite the high scientific level of this work, however, the total volume of research on inorganic chemistry in Russia before the revolution was clearly inadequate and the studies were carried out in only a few places: the chemical laboratory of the Academy of Sciences and the inorganic chemistry departments of the universities and certain higher educational establishments of other types. The grants made by the Tsarist government to the maintenance of these laboratories were negligible. There were no specialised research institutes. The number of inorganic chemists carrying out scientific research work throughout the whole of Russia did not exceed several dozen.

Decisive changes in the development of inorganic chemistry and the whole of science took place after the Great October Socialist Revolution. In Soviet Russia, among other measures designed to strengthen science, a start was made in the organisation of chemical scientific research institutes. In 1918 the Institute of Physicochemical Analysis and Institute for the Study of Platinum and Other Noble Metals were founded in the Academy of Sciences. The Central Laboratory founded by the Higher National Economic Council subsequently became the Karpov Physicochemical Institute. The Scientific Institute for Fertilisers, State Applied Chemistry Institute, the Institute for Pure Reagents, the Radium Institute, and a whole series of other research establishments were organised. Scientific research work was extended in the inorganic chemistry departments of Moscow and Leningrad universities and many other higher educational establishments. An important centre for the development of Soviet inorganic chemistry was provided by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, formed in 1934.

On the instructions of the government, the scientific research institutes and the departments of the higher educational establishments carried out extensive studies of native raw materials and methods for processing them, and helped industry to organise various new production systems, ensuring the economic independence of the young Soviet republic. The rare chemical elements were studied, and on the basis of the scientific research work which was carried out, industry organised the production of many rare metals and their compounds. Scientific research establishments were provided with pure chemical reagents, prepared in Soviet factories.

Since the time of the first five-year plans for the development of the national economy of the USSR (the years 1929–1932 and 1933–1937), the work of Soviet research chemists has been directed chiefly towards the provision of direct assistance in the task of socialist construction. In this period, inorganic chemists have developed the scientific basis for many technological processes in the chemical industry, metallurgy, and the production of binding agents.

Under the direction of N. S. Kurnakov, the salt reserves of the Soviet Union were explored, salt deposits and salt lakes were studied, and methods of natural salt technology were developed. Of particular importance was the study of the Kara-Bogaz-Gol bay in the Caspian Sea, leading to the

organisation of the industrial utilisation of its vast reserves of mirabilite. At the same time, studies were carried out on the dehydration of Glauber's salt and methods for converting it into other compounds.

Thanks to the work of N. S. Kurnakov and his coworkers, vast deposits of potassium minerals were discovered in the USSR, first around Solikamsk, and later in the Ural-Emba region of Western Kazakhstan. Studies were carried out to develop the technology of the natural potassium salts carnallite and sylvinite. In recent years the discovery of vast reserves of potassium salts in Belorussia and the construction of factories for the processing of these salts has strengthened even further the raw-material and technical basis of the Soviet potash industry.

As a result of this scientific research work and the detailed study of natural raw materials containing sodium and potassium, the Soviet Union is assured of a complete supply of compounds of these elements. Instead of importing potassium fertilisers from abroad, as was done before the revolution, the Soviet Union is now able to export these materials. At the same time the country has been provided with magnesium compounds, which have served as raw material for the production of metallic magnesium and various magnesium-containing constructional materials.

The electrochemical preparation of magnesium was studied by V. P. Il'inskii and P. F. Antipin. Studies were made of the dehydration of magnesium chloride hexahydrate, used as electrolyte for the isolation of metallic magnesium. The results of these studies provided information for the construction of magnesium factories.

In the period of industrialisation in the USSR, one of the most important technical problems was the organisation of the production of metallic aluminium from native raw material. Before the discovery of the high-grade Urals bauxites on the eve of the Second World War, the Soviet aluminium industry was based on the comparatively poor Tikhvin bauxites.

In the period 1926–1932, under the direction of A. A. Yakovkin, a large group of research workers developed methods of bauxite technology involving sintering with chalk and soda. The concentrated material was subjected to hydrometallurgical processing. As a result, the problem of the industrial utilisation of high-silica bauxites was solved successfully for the first time. Yakovkin's method was applied in the first factories of the Soviet aluminium industry—the Volkhov Aluminium Combine.

A. N. Kuznetsov and E. N. Zhukovskii put forward another method for the processing of low-grade aluminium ores, involving the high-temperature treatment of a mixture of bauxite, scrap iron, anthracite, and barium compounds. The resulting barium aluminate slag was used for the isolation of alumina. The ferrosilicon formed during the smelting is used in ferrous metallurgy. This method was introduced in the Dnepr aluminium factory.

Under the direction of P. P. Fedot'ev, the electrolysis of cryolite–alumina melts was studied, a new theory of the electrolysis of alumina was developed, and methods for the electrolytic production of aluminium under industrial conditions were devised. On the basis of this work, starting in 1932, Soviet aluminium production was organised, rapidly reaching considerable dimensions, and providing qualified personnel for the further development of this extremely important branch of industry.

Considerable work was done on the search for new forms of cement. P. P. Budnikov studied important problems related to the phenomena of dehydration, hydration, dissolution, and recrystallisation of calcium sulphate. He suggested the use of additives which could "vitalise" insoluble natural anhydrite or gypsum which had been heated at 600–750°C. On the basis of these studies, Budnikov developed a new form of binding agent—anhydrite cement—which has been widely used in constructional work. Budnikov also studied the reactions taking place during the setting of alumina cement and put forward a new form of this material—alumina cement containing added gypsum. This cement is of considerable practical importance.

Later, P. A. Rebinder, N. V. Mikhailov, and others, on the basis of the application of the methods of physicochemical mechanics to the processes involved in the setting and hardening of cements, proposed new forms of constructional materials—sand concrete and colloidal cement binding agent.

Extensive work was carried out in the Soviet Union on the chemistry and technology of phosphorus compounds. The vast deposits of apatite discovered in 1926 in the Kola peninsula were received with mistrust by Soviet industry, since the usual methods for the conversion of natural phosphates into phosphorus fertilisers proved to be inapplicable to these materials. Foreign firms, to whom specimens of the apatite ore were sent for experimental processing, rejected this form of raw material. Studies carried out under the direction of S. I. Vol'fkovich in the Scientific Institute for Fertilisers, however, established the optimal conditions for the conversion of the apatites into phosphorus fertilisers, and the Soviet Union is now assured of an unlimited supply of raw material for the production of these fertilisers, which are of the greatest importance for agriculture.

Studies were also carried out on the chemistry and technology of the rare elements.

One of the first tasks with which the Academy of Sciences was faced was the development of a method for the extraction of radium from native uranium–vanadium ores. This difficult task was successfully resolved under the direction of V. G. Khlopin, and in 1921 the workers of the Radium Experimental Factory produced a specimen of radium bromide—the first fruits of the Soviet rare elements industry. Several years later, the production of pure uranium compounds was organised in the USSR on the basis of the same raw material.

In 1922, studies on the chemistry and technology of tungsten and molybdenum were begun in the Inorganic Chemistry Laboratory of Moscow University. Some years later, this work, which was carried out by T. M. Serbin, G. A. Meerson, V. I. Spitsyn, and others, led to the organisation of tungsten and molybdenum wire production for the electric lamp industry. The creation of a basis for refractory rare metals production led subsequently to the manufacture of hard alloys based on tungsten carbide and to the preparation of other compounds of tungsten. G. A. Meerson, I. A. Shlygin, and other workers from the Moscow Electrical Factory also worked on problems associated with the production of metallic niobium and tantalum.

Under the direction of E. V. Britske, I. V. Shmanenkov, and K. Kh. Tagirov, important work was carried out in the Applied Mineralogy Institute on the utilisation of Urals titanomagnetites. This form of raw material, which is widely distributed in the Urals, cannot be subjected to ordi-

nary metallurgical processing because of its high titanium content, which leads to the formation of refractory slags in the blast furnace. At the same time, valuable amounts of vanadium were discovered in the titanomagnetites. This group of research workers proposed smelting the titanium magnetites in the blast furnace with the addition of rock salt, to give more fusible calcium sodium titanium slags and vanadium-containing cast iron. A method was developed for the conversion of the titanium slags into titanium dioxide.

M. P. Pavlov proposed another method for the processing of titanomagnetites, involving blast-furnace smelting with the use of dolomite as a flux; this also makes it possible to lower the melting point of the titanium slags and to obtain vanadium-containing cast iron. Thus the problem of the processing of titanomagnetite ores was solved completely by the persistent efforts of Soviet research scientists.

M. N. Sobolev, K. A. Bol'shakov, and N. V Krasil'nikov put forward a method, based on laboratory and pilot-plant studies, for the extraction of vanadium from the waste products obtained in the processing of vanadium-containing cast iron. The factory which was built for the production of vanadium compounds played an important role during the Great Patriotic War of 1941–1945, since it provided a complete supply of ferrovanadium for Soviet high-grade metallurgy.

Considerable work was also carried out on other, even rarer elements. Studies by E. S. Burkser and his coworkers in the Ukrainian SSR were directed towards the development of the technology of lithium, ribidium, and caesium compounds and ensured the supply of these elements.

V. I. Spitsyn and G. F. Silina in 1932 developed a method for the production of metallic beryllium and its compounds from natural raw material and organised the industrial production of beryllium.

A series of studies on the chemistry of the rare-earth elements was carried out by I. N. Zaozerskii, D. I. Ryabchikov, and others, and these permitted the production of compounds of these elements under industrial conditions.

O. A. Suvorov and his coworkers in the Kazakh SSR carried out a series of studies on the chemistry of rhenium, and this made possible the production of this metal from the waste products from the Balkhash copper smelting plant.

Work carried out in the USSR on the chemistry and technology of bromine and iodine led to the production of these elements from petroleum drilling waters on a scale sufficient to satisfy the requirements of the Soviet Union.

Outstanding studies of the chemistry of the platinum metals were carried out by L. A. Chugaev, I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, N. K. Pshenitsyn, and their coworkers.

L. A. Chugaev prepared a whole series of representatives of a new type of complex compound of quadrivalent platinum—its amido-derivatives. He worked on the hydrazine and hydroxylamine compounds of platinum, the study of which was later developed by his pupils. Chugaev also studied the physicochemical properties of the ammine complexes formed by platinum(II) nitrite and prepared the previously unknown chloropentammine.

L. A. Chugaev died very early (1922), before reaching the age of fifty. His outstanding achievement was the foundation of a research school which has carried out extremely interesting studies in the chemistry of platinum and the elements accompanying it.

Chugaev's pupil I. I. Chernyaev in 1925 discovered the "trans effect"—the most important theoretical generalisation in the chemistry of complex compounds in the last fifty years. Chernyaev established that in complexes with a square or octahedral structure the strength of the bond formed by a given ligand with the central atom depends on the nature of the ligand in the *trans*-position. This influences its replacement by other ions or molecules which are less influenced by the trans effect.

For example, a strong trans effect is shown by the nitro-group NO_2. In a study of hydroxylamine derivatives of platinum(II), Chernyaev established that in the compound

$$\begin{matrix} Cl\ NH_3 \\ Pt \\ NH_2OH\ NO_2 \end{matrix}$$

the chlorine atom in the *trans*-position relative to the nitro-group is particularly readily replaced by various radicals and neutral molecules, for example, ammonia or pyridine. In *cis*-chloronitrodiammineplatinum(II), the ammonia in the *trans*-position relative to the nitro-group is labile, whereas in *trans*-chloronitrodiammineplatinum(II) the chlorine atom is labile. The reactions with silver nitrate indicate that in the *cis*-compound the chlorine is attached by a covalent bond, whereas in the *trans*-compound the chlorine is ionic.

Atoms and molecules can be arranged in the following order of decreasing trans effect: R_2S, NO_2^-, SCN^-, I^-, Br^-, Cl^-, F^-, OH^-, . . . , RNH_2, NH_3, H_2O.

A. D. Gel'man discovered that unsaturated organic molecules such as ethylene and acetylene have a large trans effect.

The systematic occurrence of the trans effect, discovered in platinum(II) compounds, was subsequently applied successfuly to compounds of platinum(IV), palladium(II), rhodium(III), iridium(III), and cobalt(III), and various other elements.

The systematic occurrence of the trans effect makes it possible to predict the direction of reactions in the inner sphere of coordination compounds. It has therefore played an outstanding part in the development of methods for the preparation of new complex compounds. As an example, mention may be made of the work of I. I. Chernyaev and O. N. Andrianova on the preparation of the geometric isomers of the triamine $[PtBrCl(NO_2)(NH_3)En]Cl$. This complicated task was completed with the preparation of three new compounds of the six predicted by theory. The preparations involved a large number of stages and were entirely based on the use of the systematic occurrence of the trans effect.

The phenomenon of the trans effect makes it possible to develop further the ideas of A. M. Butlerov and V. V. Markovnikov on the mutual chemical influence of atoms in the same molecule. The remarkable feature of the phenomenon discovered by I. I. Chernyaev is that it is shown not by neighbouring atoms, but by ligands separated by a central atom.

B. V. Nekrasov put forward a theoretical explanation for the trans effect based on the characteristic deformability of the complex-forming atom. According to his views, the nature of the trans effect is close to the effect of ion counter-polarisation. A. A. Grinberg calculated theoretically the decrease in the strength of attraction between the

platinum(II) ion and the chloride ion, which should be observed when a second chloride ion is attached in the *trans*-position relative to the first, and showed that this effect is sufficient to produce the trans effect. Thus the trans activity of a ligand is determined by the energy of the mutual polarisation of the ligand and the central atom.

In addition to this work, a large number of mixed hexammine, pentammine, tetrammine, and triammine complexes of platinum(IV) were prepared and studied (I. I. Chernyaev and coworkers). Complexes of platinum with organic substances —pyridine, nitriles, isonitriles, etc.—were prepared.

A. D. Gel'man and L. N. Essen prepared for the first time a complex of platinum(IV) with six different inner-sphere substituents.

V. V. Lebedinskii prepared the previously unknown mono-, di-, tri-, and tetra-ammine complexes of rhodium(III), and also compounds of rhodium with thiourea. A. A. Grinberg prepared derivatives of palladium monoammines, and V. I. Goremykin prepared compounds of palladium containing hydrazine and hydroxylamine. New compounds of iridium, with thiourea in particular, were prepared. O. E. Zvyagintsev and his coworkers prepared nitrosonitrato-compounds of rutheium(II). It was shown that ruthenium is not precipitated from solutions of these substances by various reagents, which readily precipitate it from other compounds. A. M. Rubinshtein carried out extensive studies on the preparation of spectroscopically pure specimens of platinum and some of the metals accompanying it.

A. A. Grinberg and his coworkers made extensive studies of the acid–base and redox properties of complex compounds. Measurement of the dissociation constants showed that as a result of the conversion of the NH_3 molecule into the NH_2 amido-group, the ammines of platinum(IV) act as weak acids. The amidoammine complexes of platinum undergo the opposite reaction and exhibit weakly basic properties upon reaction with water.

It was found that the redox properties of ionic complexes depend not only on the nature of the central atom but also to a particularly marked extent on the nature of the ligands in the inner sphere. The appreciable lability of the inner-sphere substituents in compounds such as $K_2[PtBr_4]$, $K_2[PtBr_6]$, $[PtBr_2(NH_3)_4]$, and various others was proved by A. A. Grinberg and F. M. Filinov by isotopic exchange with radioactive tracers. On the other hand, the central atoms of the compounds studied underwent almost no isotopic exchange with corresponding ions from the solution. On the basis of this work, new analytical methods were proposed for the determination of iridium and platinum.

As a result of these studies, thousands of new compounds of the platinum metals were obtained and original methods for their preparation were developed. The development of the chemistry of the platinum metals led to improved methods for the separation and purification of these elements. Before the Great October Socialist Revolution a considerable quantity of platinum-containing raw material was mined in Russia, but the industrial refinement of platinum and the metals accompanying it were not carried out. From the work of the Chugaev–Chernyaev research school, a platinum industry was created in the USSR, producing from native raw materials all the platinum metals in a high state of purity.

A considerable amount of work on the chemistry of complexes was carried out by Ya. A Fialkov and his coworkers in the Academy of Sciences of the Ukrainian SSR. The materials studied were chiefly coordination compounds in which the central atom is non-metallic—polyhalides, polysulphides, double halides of phosphorus, antimony, and other elements, derivatives of iodine halides with organic substances, etc. A new type of complex containing iodine as cation was discovered. In the study of phosphorus halides, the existence of the tetra-acido-cations $[PCl_4]^+$ and $[PBr_4]^+$ was proved for the first time.

Systematic studies in the thermochemistry of complexes have been carried out since 1946 by K. B. Yatsimirskii and his coworkers. The heats of formation of complexes of cobalt, nickel, copper, zinc, and other transition metals (ammine, ethylenediamine, pyrophosphato-, and oxalato-complexes, etc.) have been determined. Kapustinskii's equation and other generalisations have been used to calculate for the first time the heats of formation of gaseous complex species from the gaseous components (central atom and ligands). K. B. Yatsimirskii then realised the transition from thermochemistry to the complete thermodynamic characteristics of reactions involving complex formation (the changes in enthalpy, entropy, and free energy). New methods were put forward for studying the complex formation equilibria. These include a spectrophotometric method for solutions in which several coloured complexes exist together. A kinetic method for studying the equilibria has been developed, based on the change in catalytic activities on complex formation. New methods for the mathematical treatment of data on equilibria have been proposed. A large number of equilibria in solutions of complex compounds have been studied experimentally.

There has recently been an extensive development of studies of electronic spectra and their application to the investigation of the characteristic features of the structures of complex compounds (the symmetry of the inner sphere, chemical bonding, and the fine details of the structure of the inner sphere). These methods have been applied to the complex compounds of the rare-earth elements by K. B. Yatsimirskii, N. K. Davidenko, and N. A. Kostromina. The interpretation, correlation, and generalisation of the thermodynamic, kinetic, and optical characteristics of complex compounds have been carried out on the basis of modern theoretical concepts (crystal field theory, the method of molecular orbitals, etc.).

Studies of considerable scientific value have been carried out in the chemistry of radioactive elements by V. G. Khlopin and his pupils. Khlopin's work involved chiefly the study of the laws governing the coprecipitation of radioactive elements, present in solutions at extremely high dilutions, with crystalline or amorphous precipitates separating from the solutions. Khlopin established that entrainment of the radioactive element by the crystalline precipitate takes place only if its compound is isomorphous with the substance being precipitated. The micro-component is then distributed between the crystals and the solution as a dissolved substance is distributed between two immiscible solvents. An important part is played by recrystallisation of the solid phase to achieve homogeneity and to establish equilibrium in the system with respect to the macro-component. The study of more than thirty systems containing radium, polonium, radium-D (a lead isotope), and other radioactive elements as micro-components showed that the distribution law was obeyed rigorously. Salts of barium, lead, uranium, cerium, etc. were used as the macro-component.

The Soviet radium industry has made extensive use of the practical results of the research work of Khlopin's

school. Methods for separating radium and barium have been improved considerably and new methods have been developed in the technology of radioactive substances.

This work has also led to the following conclusion: the applicability of Khlopin's law to the distribution of a micro-component in a system containing crystals and a solution of a macro-component proves that in the given instance the micro-component is isomorphous with the macro-component and replaces it in the crystal lattice. The use of radioactive tracers has thus opened up new methods for the study of the phenomena of isomorphism.

In particular, this method can be used to establish the existence of unstable compounds or compounds present in negligibly small quantities, and to study their composition and structures. In this way, V.G.Khlopin and A.G.Samartseva established that polonium forms bivalent compounds which cocrystallise with sodium telluride Na_2Te. In an oxidising medium, cocrystallisation with lead tellurate $PbTeO_4$ revealed the existence of polonate ions, corresponding to the previously unknown sexivalent polonium.

The method of "isomorphous cocrystallisation" using radioactive tracers was used by V.G.Khlopin and B.A.Nikitin to study the phenomena of so-called second-order isomorphism, in which isomorphous replacement takes place when the substances have structures of the same chemical type, irrespective of any chemical analogy. Examples include the isomorphism of barium sulphate and potassium permanganate ($BaSO_4$, $KMnO_4$), barium chromate and potassium tetrafluoroborate ($BaCrO_4$, KBF_4), sodium bromide and lead sulphide (NaBr, PbS), etc. For the example of systems containing rubidium perchlorate and radium sulphate ($RbClO_4$, $BaSO_4$), Khlopin and Nikitin showed that at concentrations of about 10^{-6}% lead and radium do not enter the crystal lattice of the perchlorates. This established the existence of a lower miscibility limit for second-order isomorphous replacement. At the same time the perchlorates studied could entrain radium or lead sulphates if the latter were present in concentrations sufficient for the construction of their own crystal lattice. This leads to a conclusion of considerable scientific importance: in true isomorphism, replacement takes place ion for ion, atom for atom, or molecule for molecule; in second-order isomorphism, however, the replacement involves complete sections of the crystal lattice, with dimensions varying from one unit cell to a comparatively large number of unit cells.

B.A.Nikitin used the principle of isomorphous cocrystallisation to study possible compounds of the inert gases. He established that sulphur dioxide hydrate $SO_2.6H_2O$, below its eutectic point (−2.6°C) absorbs radon even at a negligibly low concentration of the latter. The process obeys the distribution law. This proved that radon forms a hydrate isomorphous with the hydrate of sulphur dioxide, with composition corresponding to the formula $Rn.6H_2O$.

An analogous phenomenon was observed for other inert gases—argon and neon. The distribution constants between the gaseous phase and the solid hydrate $SO_2.6H_2O$ were different for the inert gases studied. By carrying out the separation of the sulphur dioxide hydrate in several stages and controlling the temperature, it was found possible to achieve the fractional separation of the inert gases by this chemical method.

Subsequently, B.A.Nikitin demonstrated in analogous fashion the existence of compounds of the inert gases with toluene, phenol, and *para*-chlorophenol, for example, $Rn.2C_6H_5CH_3$, $Rn.3C_6H_5OH$, and $Rn.3ClC_6H_4OH$. The molecular compounds $HBr.2C_6H_5CH_3$, $H_2S.3C_6H_5OH$, $H_2S.3ClC_6H_4OH$, etc. were used as carriers. In this way it was established that the ability of inert gases to undergo chemical reaction is not restricted to the formation of hydrates, but also extends to many organic compounds. B.A.Nikitin considered that the stability of the compounds of the inert gases which he obtained approaches that of molecular compounds. The atoms of the inert gases behave as the molecules of chemical compounds.

One of the most important ways of increasing the efficiency of the separation of elements by cocrystallisation involves the use of complex-forming reagents. This approach, pointed out by V.G.Khlopin, was developed by N.B.Mikheev and L.M.Mikheeva, who put forward equations which make it possible to calculate the degree of separation of elements under conditions of equilibrium and non-equilibrium cocrystallisation. It was shown that electrically neutral complexes can take part to only a slight extent in the cocrystallisation of ionic salts. These studies represent an extension of the thermodynamic theory of cocrystallisation, developed by A.P.Ratner, a pupil of V.G.Khlopin.

The difficulty of attaining equilibrium between mixed crystals and solution presents an obstacle to the development of multiplicative schemes for the separation of elements. V.I.Spitsyn, N.B.Mikheev, and A.Khermann developed an electrochemical method for the forced recrystallisation of sparingly soluble salts and achieved the "elution" of impurities cocrystallising with the precipitate.

The theoretical principles of the processes of ion adsorption on precipitates were developed by A.P.Ratner and V.G.Khlopin, together with V.I.Grebenshchikova and M.S.Merkulova.

M.S.Merkulova and I.V.Melikhov have recently studied non-equilibrium cocrystallisation, which is often encountered in practice. They distinguish the various stages which may limit the process, depending on the conditions of cocrystallisation.

V.I.Spitsyn and V.V.Gromov established that radioactive irradiation of the specimens influences the cocrystallisation. High radioactivity in the precipitate leads to more intensive recrystallisation, and this increases the rate of attainment of equilibrium in the system.

In addition to the study of cocrystallisation processes, studies have been made of the application of various forms of ion-exchange adsorption to the separation of radioactive elements.

Using various sorbents (glass, activated carbon, ion-exchange resins, etc.), I.E.Starik determined the state of various multivalent elements in dilute solutions.

B.P.Nikol'skii and V.I.Paramonova used the method of ion exchange to study the composition and stability of complexes of radioactive elements and isotopes. Their studies were among the first in this field.

V.I.Spitsyn and V.V.Gromov showed that the radioactive irradiation of precipitates influences their sorptive properties. The magnitude of the adsorption of basic and acidic dyes on a barium sulphate precipitate containing radium or the radioactive tracer ^{35}S, depends on the magnitude and nature of the radioactive irradiation of the isotope present; this is directly related to the electric charges produced on the surface of the solid phase, depending on whether alpha- or beta-particles are emitted.

The considerable progress made in the development of the theory of cocrystallisation and adsorption processes has found extensive technological application in the preparation of radioactive isotopes.

Soviet scientists have carried out a considerable amount of experimental and theoretical studies, covering the chemistry of the elements of all groups of the Periodic System. Only some of these can be mentioned in this brief review.

The systematic study of metal hydrides in the Soviet Union was begun by I. I. Zhukov, who showed that they can be divided into several classes—individual chemical compounds and solid solutions of hydrogen in the metals or the individual hydrides.

The preparation of the hydrides of various refractory rare metals (titanium, vanadium, niobium, and tantalum) by the reaction of the oxide of the corresponding element with calcium hydride at an elevated temperature was studied by G. A. Meerson and his coworkers.

I. A Kazarnovskii and his coworkers, on the basis of a study of the hydrides of the alkali and alkaline earth elements, calculated the radius of the negative hydrogen ion and the electron affinity of the hydrogen atom.

The hydrides of boron and the hydrides of the light and transition metals have been studied since the early nineteen-fifties by V. I. Mikheeva and her coworkers. Stable molecular compounds of diborane with pyridine, aniline, and other amines have been prepared. Optimal conditions have been established for the preparation of the alkali metal and magnesium hydrides, and also hydride halides of the type MgClH, etc. A method has been developed for the preparation of the complex tetrahydroborates and tetrahydroaluminates of various metals by double decomposition in aqueous or organic solutions, and also in salt melts. The tetrahydroborates of calcium, magnesium, and aluminium, and the tetrahydroaluminates of magnesium, cerium, and other metals have been prepared in this way.

Soon after the discovery of the heavy isotope of hydrogen, studies using deuterium were carried out in the Ukraine by A. I. Brodskii, who organised the laboratory production of heavy water as early as 1934. Brodskii and his coworkers developed an interferometric method for the quantitative determination of deuterium and carried out a number of extremely interesting studies of the isotopic exchange of hydrogen in various inorganic and organic compounds. A. I. Shatenshtein developed methods for the preparation of many deuterium compounds and carried out extensive studies of hydrogen exchange in non-aqueous solvents between various classes of substance, using their deuterium derivatives.

In the field of the rare alkali metals, mention must be made of the work of V. E. Plyushchev, who proposed new methods for the extraction of lithium and caesium from natural raw material. The study of polyhalides and double compounds with the chlorides of antimony, bismuth, and tin made it possible to improve methods for the separation of rubidium and caesium. Solid-phase reactions were used to prepare mixed compounds of rubidium, caesium, and the rare-earth elements—various zirconates, niobates, tantalates, etc.

The chemistry of beryllium has developed considerably. A. V. Novoselova, O. I. Vorob'eva, K. N. Semenenko, and others have synthesised a whole series of new fluoro-complexes of beryllium and have established the physicochemical conditions of their formation. Previously unknown crystalline modifications of beryllium fluoride, sodium fluoroberyllate, and other compounds have been discovered. New data have been obtained on the structural and chemical analogies between the fluoroberyllates and sulphates of the alkali and alkaline earth elements.

The same research team has studied the properties of beryllium nitrate and sulphate—the composition of the crystal hydrates, the thermal stability of the compounds, etc. Various covalent beryllium compounds have been prepared, and their properties and structures have been studied: these include oxide salts—the oxide formate, oxide acetate, oxide propionate, and oxide benzoate—and their compounds with various organic and inorganic molecules, alkoxy-derivatives, and compounds with ammonia and amines, nitrogen dioxide, and sulphur dioxide. Studies have been made of the properties and structures of the compounds formed by beryllium chloride with various inorganic and organic molecules, and the nature of their reactions in non-aqueous solvents.

In an investigation of natural brines containing boron, A. V. Nikolaev made a detailed study of calcium, magnesium, sodium, and potassium borates, and discovered an extremely interesting phenomenon, which has been described as borate rearrangement: when a hydrated borate is heated, the endothermic dehydration is followed by a clearly defined exothermic effect, which causes the temperature of the borate to rise spontaneously to a value which is 50–100 deg higher than the temperature of the heater. The borate rearrangement results from the crystallisation of the amorphous anhydrous borate formed initially.

B. N. Ivanov-Emin and his coworkers have carried out interesting studies on the amphoteric properties of the elements of the gallium subgroup. Acidic properties are observed in the oxides of all elements of this subgroup, but the acidity decreases sharply in the order gallium–indium–thallium, corresponding to the rules which follow from D. I. Mendeleev's Periodic Law. Sodium hexahydroxoindate $Na_3[In(OH)_6].2H_2O$, which is stable only in strongly alkaline medium, was prepared for the first time.

E. N. Deichman carried out a number of studies on the chemistry of simple and complex compounds of indium. She prepared hydrogen sulphatoindates—$H_3In(SO_4)_3$ and others—and prepared sulphato-, oxalato-, mixed sulphato-oxalato-, fluorosulphato-, and phosphato-compounds of indium. In the pre-revolutionary period, outstanding studies on the chemistry of the rare-earth elements were carried out by the Russian chemist N. A. Orlov. His last work, concerned with the isolation, by fractional crystallisation, of specimens of the least readily accessible elements of this group—holmium, dysprosium, and others—was published in the Soviet period.

Scientific research work on the rare-earth elements in the Soviet Union was held up for a considerable time by the lack of suitable raw material for their extraction. In the nineteen-thirties, considerable attention was drawn to the rare-earth minerals of the Kola peninsula, particularly lovchorrite—a titanofluorosilicate of calcium and the rare-earth elements. I. N. Zaozerskii and P. I. Protserov put forward an acidic method for its decomposition, and E. S. Burkser and G. P. Aleksandrov put forward a chlorination method. These gave the first Soviet specimens of the rare earths.

During the period of industrialisation, Soviet industry began to make extensive use of Khibiny apatites as raw

material for the production of superphosphate. The apatite concentrate contains more than 1% of rare earths of the cerium group, and this is of considerable interest in view of the large scale of phosphorus fertiliser production. S.I. Vol'fkovich and A.I. Loginova put forward a method for the extraction of rare earths from apatite during its acid conversion into concentrated fertilisers. A rare earth concentrate can be isolated by fractional precipitation from the solution using lime.

The production of compounds of the rare-earth elements permitted their study and a start to be made in their practical application. D.I Ryabchikov and E.A. Terent'eva studied complexes of the rare-earth elements with organic acids and amines. The rare-earth element in every instance showed a coordination number equal to six. The most stable compounds were obtained with tricarballylic, aconitic, nitrilotriacetic, and citric acids. Study of the last of these established the composition of the complexes—$M^{I}_{3}[M^{III}(C_6H_5O_7)_2]$, where M^{III} represents the rare-earth element. Complexes of medium stability were obtained with antipyrine, pyramidone, and pyridine as inner-sphere substituents around the rare-earth element. In the lanthanide series, the tendency to form complexes was found to increase with decrease in ionic radius.

Subsequent studies on the separation of the rare-earth elements and the preparation of their compounds in pure form developed in two directions—chromatographic methods and extraction methods. In both, an important part is played by complex formation.

L.I. Martynenko and coworkers were the first to use ethylenediaminetetra-acetic acid as eluant in the ion-exchange chromatography of the rare-earth elements. This method was used to prepare for the first time spectroscopically pure specimens of all the rare-earth elements for research organisations.

To obtain a theoretical basis for the optimal conditions for the ion-exchange separation of mixtures of the rare-earth elements, the same group made a systematic study of the composition and properties of the complexes formed by the lanthanides (Ln) with ethylenediaminetetra-acetic acid, nitrilotriacetic acid, and iminodiacetic acid. It was found that the separation generally involves mixtures of complexes. For example, when ethylenediaminetetra-acetic acid H_4A is used, complexes of the type $[LnA]^-$ and $[Ln_2A]^{2+}$ are formed, and when nitrilotriacetic acid H_3X is used, the complexes $[LnX]$ and $[LnX_2]^{3-}$ are formed. In many instances the difference in the quantities of complexes with different compositions is of greater importance for the chromatographic separation of a given pair of rare-earth elements than the difference in the stabilities of the complexes with a given composition formed by the same pair.

The study of reactions in solid-phase systems at elevated temperatures showed that the oxides of the rare-earth elements can react with the oxides of the alkali and alkaline earth metals to form compounds which are isomorphous with the analogous ferrites. Thus the manifestation of amphoteric character, previously known in this family only for scandium, has now been recognised in all the rare-earth elements (L.I. Martynenko, L.M. Kovba, and others).

L.N. Komissarova and coworkers carried out a series of studies on the chemistry of scandium. The sulphates, nitrates, oxide salts, and complexes of this element were studied. New complexes formed by scandium carbonate were prepared, and also salts of oxyacids of phosphorus in various valency states (phosphites, hypophosphite, and a number of phosphates). The results obtained were used to improve methods for the isolation of scandium from natural raw material.

N.E. Brezhneva, V.I. Levin, G.V. Korpusov, and others studied the regular features of the separation of the rare-earth elements by extraction using organophosphorus compounds. The work was originally carried out in connection with the preparation, in a state of radiochemical and chemical purity, of promethium and the radioactive isotopes of the rare-earth elements present in the waste products from the atomic industry—uranium fission products. At the same time a study was made of the mechanism of the extraction of multivalent ions by organic solvents and a direct relationship was established between the structure of the molecules of the organophosphorus extracting agents and their extracting power. The results obtained have also found application in processes for the separation of the stable rare-earth elements. The introduction of the extraction method of separation permitted the large scale isolation of rare-earth elements, in particular yttrium, with a purity of 99.9999%; this has found industrial application.

Among the inorganic compounds of carbon the carbides are important, many of them so because of their hardness and high melting point.

G.A. Meerson and his coworkers have studied the formation conditions of refractory rare metal carbides. The reduction of the oxides, for example titanium dioxide, by carbon leads to the simultaneous formation, in solid solution, of the compounds TiC, TiO, and TiN (the last of these due to the presence of residual air). The problem of preparing pure carbides is proving extremely difficult. The reduction of titanium dioxide by carbon is facilitated by using an atmosphere of hydrogen. The hydrocarbons formed apparently act as carbon carriers. When the reduction is carried out in a vacuum, a mixture of titanium dioxide and carbon gives a solid solution of metallic titanium in the carbide. It is quite probable that the phenomena observed in the formation of titanium carbide are also shown by other carbides.

In the chemistry of silicon, mention must be made of the outstanding studies of I.V. Grebenshchikov on glasses. It is known that ordinary silicate glasses contain sodium disilicate, which is fairly readily soluble in water, and calcium silicate, which decomposes fairly rapidly under the influence of acids, yet a glass containing these compounds shows an unusually high stability towards water, acids, and other chemical reagents. According to Grebenshchikov's studies, all silicate glasses react extremely vigorously and rapidly (in a period of several seconds) with water with the formation of a thin colloidal film of silicic acid on the surface; this film is produced by hydrolysis of the silicates and it prevents further decomposition of the glass. The thickness of this film has been measured by various methods and the film has been found to be extremely thin (10–60 Å).

On the basis of the properties of the surface film of silicic acid, Grebenshchikov obtained information on the part played by chemical processes in the polishing of glass. It was found that it is not the hardness of glass, but its chemical stability, which primarily influences the rate of grinding and polishing. Change in temperature, the introduction of substances into the solution which are adsorbed by the protective film of silicic acid, and the replacement of water by other liquids all have a marked influence on the

thickness and properties of the protective film, and hence on the process of glass polishing.

A whole range of silicate systems has been subjected to detailed study by modern physical and physicochemical methods. On the basis of the research work carried out under the direction of I. V. Grebenshchikov and N. N. Kachalov, the production of first-class optical glass was organised in the USSR in the late nineteen-twenties.

Recently, N. A. Toropov and his coworkers have studied silicate systems containing the rare earths and other refractory oxides.

A large number of studies have been carried out by E. I. Gladyshevskii and his coworkers on the silicides and germanides of various metals. Studies have been made of binary and ternary systems containing vanadium, chromium, manganese, iron, cobalt, nickel, titanium, the rare-earth elements, and many other metals. It is only in a few instances that the compositions of the compounds obtained are determined directly by the main valencies of the components, and for the most part the compositions are determine by geometric and electrochemical factors and the degree of electron delocalisation. The compounds obtained include La_3Si_2, Lu_5Ge_3, VCoSi, $CaAl_2Si_2$, $Mo_5Co_3Ge_2$, etc. In the formation of silicides and germanides, an important part is played by the formation of covalent Si–Si and Ge–Ge chains.

Work on the chemistry of zirconium and hafnium has continued to develop. L. N. Komissarova, Yu. V. Granovskii, and others have studied the processes involved in the separation of these elements by extraction using tributyl phosphate; methods involving mathematical planning of the experiments were used. In the same laboratory, studies have been made of the solid-phase reactions between hafnium dioxide and oxides of the rare-earth elements.

N. A. Godina and others have studied the reaction of zirconium dioxide with the rare-earth elements and of hafnium dioxide with the alkaline earth elements; this has given more accurate information on the equilibrium diagrams for these systems.

Yu. V. Khodakov has shown experimentally that all previously proposed schemes for the hydration of phosphorus(V) oxide are erroneous, since they do not make allowance for the formation of intermediate products—higher polyphosphoric acids: the tetra-acid $H_6P_4O_{13}$ and the tri-acid $H_5P_3O_{10}$. The mechanism established for the hydration of phosphorus(V) oxide corresponds to the theory of the three-dimensional structure of the anhydrides of the oxo-acids, developed by Yu. V. Khodakov.

A. V. Lapitskii has published a number of studies of the chemistry of niobates and tantalates. In particular, he has made a detailed study of the dependence of the dehydration and thermal stability of these compounds on the nature of the cations present.

There has been a considerable increase in information on peroxo-compounds. I. A. Kazarnovskii and his coworkers have studied a new class of oxygen compound of the alkali metals—ozonides—obtained by the action of ozone on the correspoinding hydroxides. The products of the side-reactions were previously known, but the substances obtained in this instance could be isolated in pure form only because of the original method employed—extraction by liquid ammonia. A detailed chemical study was made of potassium ozonide; its structure was studied by X-ray diffraction and magnetic methods, and its heat of formation was measured. It was shown that the structure of potassium ozonide is given by the formula $K^+O_3^-$. Study of the isotopic exchange of oxygen between KO_3 and water enriched in $H_2{}^{18}O$ gave new data on the reactivity of the free hydroxyl radical. A mechanism for the reaction of ozone with alkalis was proposed on the basis of these studies.

Compounds of sulphur, selenium, and tellurium have been widely studied, since they are of considerable interest as semiconducting materials. A. V. Novoselova and coworkers prepared and studied the electrical properties of the binary and some ternary chalcogenides of titanium, zirconium, vanadium, niobium, tantalum, and other metallic elements. Semiconductors and dielectrics have been found among chalcogenides with general formula $A^{II}B^{IV}C_3^{VI}$. The change from dielectrics to semiconductors is accompanied by a change in structural type. The thermal stabilities of a number of selenides and tellurides have been studied. The equilibrium diagrams of the Ge–S, Ge–Se, and other systems have been obtained in fundamental studies on the preparation of semiconducting compounds.

Important studies on the preparation of various arsenides and antimonides have been carried out by N. A. Goryunova.

In the chemistry of the oxygen compounds of sulphur, mention must be made of the interesting derivatives of sulphamic acid prepared by A. V. Kirsanov: *N*-(chlorosulphonyl)phosphorimidic trichloride $ClSO_2.NPCl_3$, sulphanuryl chloride $(NSOCl)_3$, etc.

V. I. Spitsyn and his coworkers have carried out a number of studies on the chemistry of tungsten and molybdenum. The compositions of the isopolytungstates and isopolymolybdates formed by various metals have been established. Detailed study of the dehydration of many aquopoly- and heteropoly-compounds has shown the important constitutional role played by water in these substances. At the same time the use of tracer atoms has established the high mobility of its molecules in these compounds. Isotopic and ion exchange between the anions of various heteropolyacids has been studied. The simultaneous use of two radioactive tracers (^{32}P and ^{185}W) made it possible to establish, by the self-diffusion method, that the reaction between the anions of two acids capable of forming a heteropolycompound (for example, HPO_4^{2-} and WO_4^{2-}) begins even in the alkaline range and apparently involves hydrogen bonding. A new coordination treatment of the structure of aquopoly- and heteropoly-compounds has been put forward, based on oxonium groups and hydrogen bonding, the molecules of the corresponding acids, for example, H_2MoO_4 and H_2WO_4, being regarded as inner-sphere ligands.

E. A. Nikitina has studied problems associated with the preparation of heteropolycompounds and has proposed a method, which does not involve the use of ether, for preparing molybdophosphoric, molybdosilicic, and tungstophosphoric acids by the direct reaction of the corresponding reagents, for example, phosphoric acid and molybdenum(VI) oxide.

A. I. Kokorin and coworkers have studied tri- and tetraheteropolyacids and have prepared a number of new representatives—vanadomolybdophosphoric, tungstomolybdosilicic, vanadotungstomolybdophosphoric, and other similar acids.

Z. F. Shakhova and R. K. Motorkina have studied heteropolycompounds of germanium and certain rare-earth elements. They showed by various methods that the structures of the reduced and non-reduced forms of tungstogermanic and molybdogermanic acids are identical.

V.I. Spitsyn, V.F. Chuvaev, and V.Ya. Kabanov applied proton magnetic resonance to the problem of the basicity of heteropolyacids. According to the Miolati–Rosenheim theories, the central atom in these acids always has a coordination number of six, so that, for example, a high basicity, equal to seven, was assumed for molybdophosphoric acid: $H_7[P(Mo_2O_7)_6]$. X-Ray diffraction studies by Keggin and others led to the conclusion that the usual coordination number of phosphorus and silicon in heteropolyacids is four. The basicity of the heteropolyacids should then be lower; for example, the formula for molybdophosphoric acid should be $H_3[PO_4(MoO_3)_{12}]$. Chemical studies generally did not confirm the formation of salts with a high degree of substitution. The problem remained open, however.

The method of nuclear magnetic resonance makes it possible to distinguish the states of hydrogen atoms in compounds and to decide whether they correspond to H^+, OH^-, H_3O^+, or H_2O. The use of this method established unambiguously that the number of hydrogen ions in ordinary heteropolyacids corresponds to the low basicity which follows from their X-ray diffraction study. Thus the suggestion that there exist salts of heteropolyacids with a high degree of substitution should be rejected.

Simple and complex fluorides have been studied for a number of years by I.V. Tananaev and his coworkers, who were the first to prepare sodium hydrogen fluoride and lithium hydrogen fluoride. The hydrogen hexafluoroaluminates $AlF_3.3HF.6H_2O$ and $AlF_3.3HF.3H_2O$, previously unknown in the free state, have been prepared; these compounds have been described as cryolitic acids. The same group of workers have studied many double fluorides formed by metals. Natural cryolite has been found to have the composition $11NaF.4AlF_3$, and not $3NaF.AlF_3$, as previously assumed. Interesting data have been obtained on the stepwise electrolytic dissociation of the fluoride of multivalent elements.

I.V. Tananaev and his coworkers have also used various physicochemical methods to study heavy metal hexacyanoferrates(II) and the double salts which they form with alkali metal hexacyanoferrates(II). Double potassium–nickel, potassium–cobalt, caesium–cobalt, and other hexacyanoferrates(II) have been isolated for the first time. The compositions of the double hexacyanoferrates(II) formed by potassium with indium and gallium have been established: $KIn[Fe(CN)_6]$ and $KGa[Fe(CN)_6]$. This type of compound has proved to be characteristic for tervalent metals and is usually formed instead of the normal hexacyanoferrates(II). Analogous results were obtained for lanthanum hexacyanoferrates(II). A hexacyanoferrate(II) method has been proposed for the separation of yttrium from cerium and lanthanum. The use of the radioactive silver tracer ^{110}Ag has made it possible to study the replacement of the alkali and heavy metal in various simple and mixed hexacyanoferrates(II) by silver ions and hence to characterise the relative strengths of the bonds formed by the metals in the outer sphere with the hexacyanoferrate(II) ion.

Mention must also be made of the fact that Soviet inorganic chemists have paid considerable attention to the development of the chemistry of the little-studied radioactive elements. V.I. Spitsyn and A.F. Kuzina developed methods for isolating the long-lived isotope of technetium ^{99}Tc from neutron-irradiated molybdenum. These authors prepared various technetium compounds and studied their properties. In the same laboratory, R.A. D'yachkova studied the isolation of protoactinium from the waste products from the processing of uranium ores and for the first time in the Soviet Union obtained ponderable quantities of this element. The forms in which protoactinium exists in aqueous solutions with different acidities have been studied.

After the organisation of an atomic industry in the USSR, research workers were able to study the chemistry of plutonium and other transuranium elements. V.V. Fomin and coworkers showed that in addition to the fluoride $NaPuF_5$ described in the literature, compounds M_2PuF_6, where M = Na or NH_4, exist. Measurement of the vapour pressure of plutonium tribromide in bromine vapour established the formation of plutonium tetrabromide, unstable at low temperature. A detailed study was made of the decomposition of oxalates of plutonium under the influence of its own radiation, leading to the conversion of the oxalates into carbonates and reduction of plutonium. This change in the specimens readily explains their appreciable solubility in acids after they have been kept for some time. Other simple and complex compounds of plutonium were prepared and studied.

A.D. Gel'man, A.I. Moskvin, V.P. Zaitseva, M.P. Mefod'eva, and others have studied complex formation of neptunium, plutonium, americium, and curium in aqueous solutions with various ligands. The stability constants of the ionic complexes have been determined. The kinetics of the valency changes in neptunium and plutonium in nitric acid solutions have been studied, and the influence of complex formation on the redox reactions of these elements has been investigated.

A large number of simple and complex compounds of neptunium and plutonium have been isolated by these authors and characterised in the solid state. Examples include $M_4Np(C_2O_4)_4.nH_2O$, $NpO_2C_2O_4.3H_2O$, and the plutonium(V) compounds $NH_4PuO_2F_2$, $NH_4PuO_2CO_3.3H_2O$, $NH_4PuO_2HPO_4.4H_2O$, $(NH_4)_2PuO_2(OH)CO_3.nH_2O$, and $NH_4[PuO_2C_2O_4].6H_2O$. Pure concentrated solutions of tervalent uranium have been prepared, and various complex compounds have been isolated in solid form from these solutions.

V.M. Vdovenko and coworkers have made a number of studies of complex formation by uranium and plutonium in connection with methods for their separation by extraction. Nitrato-, sulphato-, chloro-, and other complexes have been studied. Tributyl phosphate, diethyl and dibutyl ethers, and various amines have been used as organic media. The structures of various compounds of uranium and plutonium have been established by infrared spectroscopy and proton magnetic resonance.

A traditional field of Soviet inorganic chemistry is the study of metallic alloys and the chemical compounds which they form.

N.S. Kurnakov, G.G. Urazov, and their coworkers have prepared many new alloys based on magnesium and aluminium, and have established their structures. This has made it possible to organise the production of most important materials for the aviation industry and other branches of the national economy.

Studies of heat-resistant alloys based on iron and chromium, carried out by I.I. Kornilov, have made it possible to produce new and valuable materials for high-temperature technology. V.A. Nemilov has prepared a whole series of palladium alloys which had not been studied before. E.M. Savitskii has studied the properties of alloys based on the rare-earth metals. In connection with problems associated with light alloys, A.V. Novoselova, N.D.

Nagorskaya, and others studied for the first time the equilibrium diagram of the Al–Be–Mg system, and also investigated the nature of crystallisation in beryllium-rich alloys of various systems (Be–Nb and Be–Re).

A series of important studies has been carried out by A. F. Kapustinskii on the dependence of the energetics of chemical reactions on the positions of the elements in the Periodic System. He made a systematic survey of the thermodynamic properties of the sulphides of various metals, and put forward a convenient simplified equation for calculating crystal lattice energy as a function of the valencies and radii of the ions forming it.

A valuable contribution to the thermodynamics of inorganic compounds, particularly the halides and oxides of the rare elements, was made by the work of S. A. Shchukarev.

The theoretical principles of chemical bonding in inorganic compounds has been developed by Ya. K. Syrkin and M. E. Dyatkina. A theory of directed valencies and a theory of the valency states of atoms in molecules have been developed, and the interactions of atoms with electrons have been studied from the viewpoint of quantum mechanics. Systematic studies of the valency states of both transition and non-transition elements have made it possible to reach a number of conclusions of importance for inorganic chemistry. In particular, the electronic structure of the tetrahedral oxoanions of the transition metals has been studied. Quantum-chemical calculations of the energies of inorganic compounds have made it possible to make predictions regarding the covalent character of the bonding in crystals; this is extremely significant for an understanding of the semiconducting properties of various inorganic substances.

---o0o---

In the fifty years for which the Soviet State has been in existence, inorganic chemistry has grown in the Soviet Union, together with the whole of chemical science. As can be seen from this necessarily brief review, considerable progress has been made in many important fields of the development of modern inorganic chemistry. However, the great task which stands before us—the construction of communism by the first workers' state in the world—is increasing to an even greater extent the need for the extensive utilisation of science as a direct productive force in society. The potential possibilities provided by inorganic chemistry in this respect are unusually great: inorganic polymers, laser crystals, refractory and super-hard materials, materials for superconductivity, and many other valuable materials can be provided only by inorganic chemistry.

Our country's anniversary is inspiring Soviet inorganic chemists to new scientific efforts and achievements!

U. D. C. 547

SOVIET ORGANIC CHEMISTRY AFTER 50 YEARS

N. S. Zefirov

Russian organic chemistry long ago won an honourable place in world science. The names of A. M. Butlerov, V. V. Markovnikov, N. N. Zinin, E. E. Vagner, and N. N. Men'shutkin have acquired a wide repute. Russia had strong chemical schools; in this connection special mention must be made of the Kazan' chemical school, which has produced a great number of brilliant organic chemists, to whom world science must be obliged for the greatest scientific achievements.

Despite this, it has fallen to the Soviet land after half a century to make the most grandiose work on the development of chemical science and industry. Before the revolution chemical science had developed only in individual scientific centres and the number of chemists with higher education amounted to not much more than 1000; the organic chemical industry was practically non-existent.

Fifty years later a powerful chemical industry has been created in our country. In the USSR a series of new means of production—coal tar chemicals, aniline dyes, petrochemical, chemico-pharmaceutical, etc.—have been set up where there was literally an empty place. This enormous construction required great forces in assimilating even the experience gained abroad. In addition our country developed novel solutions for various problems in the construction of a chemical industry. The clearest example is the organisation of the production of synthetic rubber, which was the first in the world.

The rapid development of the organic chemical industry in the USSR was based on the experience and traditions of Russian, and then Soviet, organic chemistry. On the other hand, with the development of the chemical industry, organic chemistry obtained a new firm foundation. After years of Soviet power, having opened wide the doors of educational establishments, there grew up in our land an enormous army of organic chemists. A marked extension of the "geography" of organic chemistry resulted—in addition to Moscow, Leningrad, Kazan', Kiev, Tomsk, Khar'kov, Odessa, and Riga, there are now large scientific centres at Gor'kii, Kuibyshev, Novosibirsk, Irkutsk, Vladivostok, Erevan, Tbilisi, Baku, Tashkent, etc.

It is impossible to list all who took part in this. We will only note that during the years of Soviet power new scientific schools have developed which are of worldwide repute and which determine the development of individual branches of organic chemistry not only in our own country but throughout the world. In this connection mention must be made of the school of N. D. Zelinskii, who tackled many problems of the chemistry of hydrocarbons and organic catalysis; the school of A. E. Favorskii and S. V. Lebedeva, who developed the chemistry of unsaturated aliphatic compounds; the school of A. E. Chichibabin, celebrated for their investigations in the field of heterocyclic compounds; the school of A. N. Nesmayanov, who worked at large classes of organoelemental compounds and moulded this division of organic chemistry into an independent field; the school of A. E. Arbuzov, whose studies in the field of the chemistry of organophosphorus compounds are well known.

The basis of organic chemistry, as for any other science, are its theoretical concepts. Russian chemists have always paid special attention to the fundamental rules. It is sufficient to name A. M. Butlerov, who created the structural theory, V. V. Markovnikov, well-known for the principal investigations into problems of the mutual interaction of atoms in a molecule, N. N. Menshutkin former pioneer of the use of kinetic methods of investigation in organic chemistry. This tradition lives on today.

A distinguishing feature of modern organic chemistry is the wide use of methods of mixed sciences—physics and biology. Undoubtedly the achievements of Soviet chemists