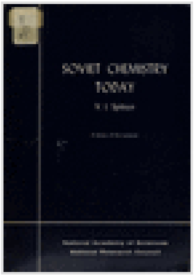

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The exchange of scientists between the U.S.A. and the U.S.S.R. under the terms of the Bronk-Nesmeyanov agreement is an encouraging development. World War II interrupted the relatively easy international travel of scientists and the easy exchange of basic scientific information for many years. Since the war, many of the prewar conditions have been restored, but between the western nations and the U.S.S.R. impediments to the exchange of views in print and in person have remained greater than is best for our common good. Part of the impediment is traceable to language difficulties. We in American science have not until recently taken seriously enough the necessity for many of us to master the Russian language, which now must be regarded as one of the foremost languages of science. Part of the difficulty is traceable to the Russian system of research progress journals which are not all known or available in our country. The visit of Academician V. I. Spitsyn to the United States provided those of us who heard his lectures or talked with him privately the opportunity to get well briefed on the status of important Russian work in the fields of chemistry, radiochemistry, radiation chemistry and related fields. I am pleased that Professor Spitsyn has courteously extended permission for the publication of his lectures so that their valuable contents may be more widely available to American scientists.

Glenn T. Seaborg
U.S. Atomic Energy Commission

SOVIET CHEMISTRY TODAY

Its Present State and Outlook for the Future

V. I. Spitsyn

Active Member of the U. S. S. R. Academy of Sciences
Director, Institute of Physical Chemistry, Academy of Sciences, U. S. S. R.

A Series of Six Lectures

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6. Study of Chelate Compounds in the U. S. S. R.

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INTRODUCTION

On July 9, 1959, Dr. Detlev W. Bronk, President of the National Academy of Sciences of the U. S. A., and Academician A. N. Nesmeyanov, President of the Academy of Sciences of the U. S. S. R., signed an agreement providing for exchange visits by research scientists of each country. The agreement between the two Academies is part of a program of cultural, technical, and educational exchanges between the two countries provided for under the Lacy-Zaroubin agreement whose signing in 1958 was hailed by the U. S. State Department as a "significant first step in the improvement of mutual understanding between the peoples of the United States and the Union of Soviet Socialist Republics".

Among the distinguished Soviet exchange visitors was Academician V. I. Spitsyn, and it was the privilege of the Division of Chemistry and Chemical Technology and of the Office of International Relations of the National Academy of Sciences—National Research Council to arrange for Professor Spitsyn's stay in the United States. Those who had an opportunity to visit with Professor Spitsyn can hardly have failed to appreciate his sincere desire to further the aims of the Bronk-Nesmeyanov agreement. During the course of his visit Professor Spitsyn specifically requested that the text of the lectures he presented be made available on a wide basis to American scientists as his personal contribution to the promotion of better mutual understanding between the two countries.

The National Academy of Sciences—National Research Council is pleased to comply with Professor Spitsyn's gracious request and sincerely hopes that these printed lectures will be of as much value to those who read them as the spoken lectures were to those who heard them.

The inter-Academy exchange program, under which Professor Spitsyn visited the United States, is supported by a grant to the National Academy of Sciences from the National Science Foundation. Publications of Professor Spitsyn's lectures has been made possible through the support of the United States Atomic Energy Commission.

Particular acknowledgment should be extended to Professor W. W. Meinke and his associates in the Department of Chemistry at the University of Michigan, who undertook the substantial task of editing the present volume for publication in the United States.

Robert C. Elderfield, Chairman
Division of Chemistry & Chemical
Technology

CHEMICAL SCIENCE IN THE U.S.S.R.

Its Present State and Outlook for the Future

V. I. Spitsyn

The beginning of this century saw a rapid rise in the role of the chemical industry in the national economies of the technically advanced countries. Its growth began to overtake the development of other important branches of production, such as ferrous metallurgy. This was attended by a flourishing growth of many fields of chemical science.

Pre-revolutionary Russia had an underdeveloped chemical industry that did not ensure the basic economic requirements of the country and its defense. The proportion of basic chemistry -- the production of acids, alkalis, and salts -- was very low. Many important chemical products were imported from other countries, although their production could have been organized on the basis of raw material within the country. For instance, the coking of coal was, as a rule, carried out without utilizing any by-products. And at the same time, phenol, benzene, naphthalene and other such valuable materials were imported from other countries, as also were intermediates for the production of pharmaceutical preparations, organic dyes and even explosives.

Serious drawbacks likewise characterized the development of chemical science. Pre-revolutionary Russia had many brilliant chemical names, including D. I. Mendeleyev, N. N.

Zinin and A. M. Butlerov. But the total number of chemical scientists was small, and for this reason only a small number of isolated scientific trends were under development. Research was conducted mainly by a few chairs of chemistry in higher educational institutions. The number of specialized laboratories was insignificant, and there were no chemical research institutes at all.

The situation changed radically after the Great October Socialist Revolution of 1917. Despite the difficulties due to civil war, the Communist Party of Russia and the Soviet Government set out immediately with the task of developing Soviet science according to plan. Science was to become the basis for a radical reconstruction of the backward economy of pre-revolutionary Russia, which, in addition, had suffered greatly as a result of the First World War and the counter-revolutionary intervention of a number of foreign states. At the beginning of 1918, Lenin personally compiled the program of scientific-technical work on the most important problems of the national economy. Organizational work was started on a number of research institutes, including many in the field of chemistry.

In 1918, an Institute of Physico-Chemical Analysis and an Institute for the Study of Platinum and Other Precious Metals were established as adjuncts to the Russian Academy of Sciences. The Central Laboratory, which was established as part of the Supreme Council of the National Economy, was later transformed into the Karpov Physico-Chemical Institute. These were later followed by the Scientific Institute of Fertilizer, the State

Institute of Applied Chemistry, the Institute of Pure Chemical Reagents, the Scientific Chemico-Pharmaceutical Institute, the Radium Institute, the Scientific Institute of Organic Intermediates and Dyes, the Institute of Artificial Fibres, the Institute of Synthetic Rubber, and many others. The chemical departments of higher educational institutions greatly expanded their research programs. At the present time, the Soviet Union has about 800 research institutions in the field of chemistry, not counting factory laboratories.

A serious problem was that of training scientific and technical personnel in chemistry. In 1913, Russia could number not more than a thousand chemists with higher education. After the 1917 Revolution the broad establishment of a network of chemical departments, chemico-technological institutes and other specialized higher educational establishments made it possible to increase the output of chemists of highest qualification and diverse specialization by tens and hundreds of times. At present, the U.S.S.R. has hundreds of doctors of Science (professors), thousands of candidates of Science, and tens of thousands of chemical engineers and research chemists representing a huge army that is capable of resolving the most complex problems of present-day chemical science and industry.

Great attention is being devoted to construction work in the chemical industry. The very first plan for the development of the national economy of the Soviet Republic, compiled by the State Commission on the Electrification of Russia (GOELRO) in 1920, in the midst of civil war and intervention, provided for an accelerated development of the chemical industry as compared with other branches of industry. In 1928 the Soviet Government passed a special resolution on measures to introduce chemical methods into the national economy of the country; in this process, chemistry was regarded as one of the decisive factors in the industrialization of the national economy.

Soviet chemical industry was on the upsurge during the first five-year plans of our country. In 1932 the level of its gross output had already more than 4.5 times topped the chemical output in pre-revolutionary Russia. It is particularly important to note that the Soviet chemical industry with all its complex branches was actually built anew and began to function on the basis of the latest and most advanced methods of technology. The chemical industry continued its steady growth over subsequent years too.

During the period of the Great Patriotic War, the Soviet chemical industry was putting out at least 20 times more goods than the pre-revolutionary industry. Soviet chemistry played an important part in the defeat of fascism, fully supplying the needs of the front and the rear as regards chemical materials. During the post-war period, rehabilitation and development of the chemical industry went ahead at a fast pace. The prewar level of chemical production was exceeded in 1950 by 80 per cent; by 1955 it had topped the prewar level more than three times over. In 1957, the output of the Soviet chemical industry was 112 times that of pre-revolutionary Russia in 1913. The Soviet chemical industry expanded immensely the assortment of chemical goods, introduced the finest methods of synthesis and processing of the most complex types of raw material; it created an industry for the cracking of oil, the production of motor fuel, and synthetic additives to it, and of lubricants; it created an industry of aromatic raw materials and the synthesis, on this basis, of a number of valuable products (dyes, explosives). Also organized was chemico-pharmaceutical production, an industry of synthetic rubber, artificial and synthetic fibres, plastics, and many others. At the present time, the U.S.S.R. is producing all the rare metals that find application in industry. Recent years have seen the creation of a radiochemical industry that is supplying the national economy with fissionable materials for the generation of atomic energy and numerous radioactive isotopes. Yet even these rapid strides in the development of chemistry have not satisfied the demands of the Soviet Union.

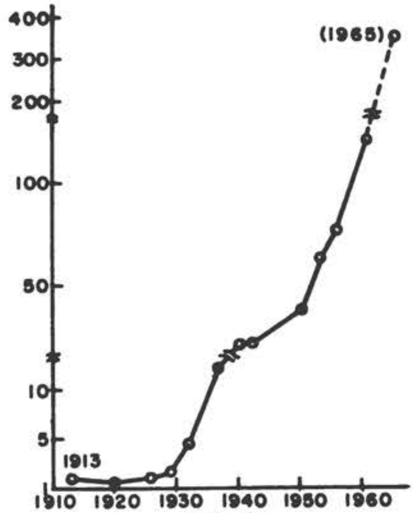


Fig. 1 Growth of the chemical industry of the USSR (1913 = 1).

In 1958, the Soviet Government considered specially the problems of further development of the chemical industry. Once again its great importance in the development of the economy of the country and of all other branches therein was stressed. Particular attention was devoted to problems of expanding the production of synthetic high-polymer materials for use in the output of consumer goods and for industry. This found its reflection in the seven-year plan for the development of the national economy of the U.S.S.R. during 1959-1965. The control figures of this plan involve many important chemical problems. The seven-year plan also provides for an enormous growth of the chemical industry proper. During this period, the total volume of annual output will increase by roughly three times and will thus exceed the chemical production of pre-revolutionary Russia of 1913 by 300-350 times. Capital investments in the chemical industry will amount to 100-105 billion rubles. Over 140 large chemical plants will be built anew or completed. Over 130 plants are to be reconstructed. The construction of the new plants and the reconstruction of operating plants of the chemical industry will proceed on the basis of a broad utilization of the attainments of science and technology both in our country and abroad. The production of synthetic materials will experience particular development. The output of artificial fibres will increase 4 times, and the most valuable of them (synthetic fibres) 12 or 13 times. The production of plastics and synthetic resins will go up over 7 times. Fabrics and furs made of artificial fibres, synthetic leather on the basis of polymer films, plastics for the manufacture of other valuable articles will begin to play an increasingly important role in satisfying the demands of the population and the requirements of industry and other branches of the national economy of the U.S.S.R.

The control figures of the seven-year plan provide for a considerable development likewise in the other divisions of the chemical industry. The output of mineral fertilizers will increase roughly 3 times. There will be an increase in the production of new types of concentrated fertilizers, preparations for fighting agricultural pests and diseases, and also chemical weed-killers.

The problem confronting all branches of the chemical industry is the maximum mechanization of production processes, automation of control and the development of new corrosion-resistant constructional materials for the manufacture of apparatus. In this field of chemical science the most important problem is the utmost expansion of theoretical investigations to promote the development of new and improved technological processes and the creation of synthetic materials with properties that will satisfy the demands of today's industry.

The scientific level and practical potentialities of our chemical science are based on the results of the tremendous work carried out by the chemical scientists of the U.S.S.R. in the past 43 years of Soviet power. At present the front of research in chemistry embraces, to a greater or lesser extent, all spheres of chemical science. In this review, which is necessarily brief, I shall consider only the most important results of research that characterize the present state of chemical science in the U.S.S.R.

In the field of inorganic chemistry, the first five-year plans saw the carrying out of extremely valuable work associated with the study of sodium and potassium salts and methods of extracting them from raw materials within the country. As far back as 1916, N. S. Kurnakov appreciated the significance of utilizing the enormous reserves of sodium sulphate in the Kara-Bogas-Gol Bay in the Caspian Sea, pointing out that "a study of methods of utilizing this substance represents one of the basic problems of Russian chemical technology." Extensive research begun in 1921 made possible a comprehensive investigation of Kara-Bogas-Gol and preparations for industrial application of its immense supplies of mirabilite. At the same time, Kurnakov and his co-workers made extensive investigations into salt equilibria that lead to the formation of mirabilite from sea water, the separation of soda from the brines.of sulphate-soda lakes, etc. Studies were made of the conditions of dehydrating Glauber salt, and rational methods were developed for the use of sodium sulphate in the chemical industry.

Particularly important was the role played by Kurnakov and his school in the building up of the Soviet potassium industry. Studies of numerous samples of salts and brines taken from drill holes in the vicinity of Solikamsk led to the conclusion that potassium compounds were present in the salt deposits of this area. These conclusions were confirmed in 1925 by drilling that culminated in the discovery (under the supervision of P. I. Preobrazhensky) of one of the largest deposits of potassium salt - Solikamsk (and also of sodium and magnesium salts).

On the basis of an enormous amount of experimental material amassed in studies of the conditions of crystallization of various water-salt systems, N. S. Kurnakov, G. G. Urazov, A. G. Bergman, N. N. Efremov and their colleagues theoretically considered the conditions of the precipitation of salts in the evaporation of sea water, for instance from the ancient Perm Sea that existed about 200 million years ago in the east of the European part of the U.S.S.R. and that extended from the Arctic Ocean to the Caspian Sea. It was suggested that besides the Solikamsk area, new potassium deposits should be sought for on the eastern boundaries of the Perm basin (Lake Inder, near the mouths of the Ural and Emba Rivers).
Several years later these suppositions were brilliantly confirmed by the discovery of deposits of potassium salts in the Ural-Emba region. Later, many other deposits of potassium salts were discovered in the U.S.S.R. and this country now occupies first place in the world in reserves of potassium salts. At the same time, N. S. Kurnakov, N. I. Stepanov and other investigators devoted much attention to the theoretical development of methods of physico-chemical analysis of multicomponent systems, which has seen such fruitful use in the study of salt equilibria. Subsequently, Soviet scientists introduced into the study of the physico-chemical diagram the element of time, which led to the development of the kinetic

method of physico-chemical analysis. It may be stated that the Soviet school of physico-chemical analysis is one of the greatest in the world.

As a result of the discovery, in 1925 by expeditions of the U.S.S.R. Academy of Sciences under the leadership of A. E. Fersman, of enormous deposits of apatite-nepheline ores in the Khibin mountains on the Kola Peninsula, the Soviet Union obtained new supplies of a valuable mineral. Investigations carried out in the Scientific Institute of Fertilizers under the supervision of S. I. Volfkovich made it possible to establish the optimum conditions for the chemical processing of apatites, which proved to be a very complicated problem: foreign firms that were given samples of the apatite ores for a trial processing pronounced it unsuitable. At the present time, apatite concentrates are successfully utilized to obtain phosphoric fertilizers, phosphoric acid, fluoride salts and other products. The nephelines that accompany apatite were also put to use for the production of alumina, soda, potash, cement, and other products (I. A. Talmud, N. I. Vlodavets, F. N. Strokov, and others.).

In the U.S.S.R., a research study was made of utilizing the method of obtaining synthetic ammonia and its various derivatives and also nitric acid by means of oxidizing ammonia. On the basis of these investigations, large nitrogen-fertilizer factories (Bereznikovsky, Kemerov, Stalinogorsk, Chirchik, and others) have been built, that fully supply the Soviet Union with nitrogen compounds. M. I. Temkin, I. P. Sidorov, and others have carried out important investigations into the kinetics of the synthesis of ammonia. They proposed the following equation for the rate of this reaction:

$$V = K_1 P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}} \right)^{\alpha} - K_2 \left(\frac{P^2_{NH_3}}{P_{H_2}} \right)^{1-\alpha} ,$$

where K_1 is the constant of the rate of synthesis, K_2 is the constant of the rate of decomposition of ammonia, P is the appropriate partial pressure, and α is a constant factor. In deriving the equation, the gases were considered to be ideal; under high pressures, volatility of the gases enter into the equation in place of the partial pressures.

This equation is applicable if the system is in a state close to equilibrium. With a small quantity of ammonia, its synthesis proceeds at a rate proportional to the pressure of the nitrogen, according to the equation of the first order. Alteration of the order of the reaction is due to a change in the degree of surface coverage with adsorbed nitrogen. Variations in the rate of synthesis and decomposition of ammonia on different catalysts have shown that the process obeys the foregoing equation with the value of $\alpha = 0.5$. Thus, adsorption of nitrogen and its desorption are limiting stages of the processes of formation and decomposition of ammonia.

Large-scale investigations have been carried out by Soviet chemical technologists jointly with agricultural chemists in the development of new and the refining of existing methods of obtaining nitrogen-concentrated and complex fertilizers (D. N.

Pryanishnikov, E. V. Britske, S. I. Volfkovich, and others).

Problems of the chemistry of sulphuric acid and the mechanism of its reactions of formation have likewise engaged Soviet researchers. K. M. Malin has made a study of the rate of oxidation of sulphur dioxide in the liquid phase of tower systems in the absence of oxygen, and has found that it increases with increasing content of sulphur dioxide, enhanced concentration of nitrogen oxides, and increased water content. The maximum rate of oxidation is attained when sulphur dioxide is absorbed by 57.6-per cent sulphuric acid in which nitrosyl sulphuric acid is totally hydrolyzed. The dependence of the rate of oxidation on the linear rate of the gas, the density of irrigation and the temperature has been studied by I. N. Kuzminykh.

As a result of a deep study of the theory of the oxidation process of sulphur dioxide and the advancement of the technological regime to optimum, the output of tower systems of the sulphuric acid factories of the Soviet Union increased several times over within a short time.

Soviet scientists have made a big contribution to the chemistry of precious metals. As far back as pre-revolutionary times, L. A. Chugayev engaged in a systematic study of the complex compounds of platinum. His studies expanded particularly after 1917. Chugayev synthesized a whole series of representatives of the new type of complexes of tetravalent platinum - its amide-derivatives. He likewise made a study of hydrazine and hydroxyl-amine compounds of platinum, synthesized the hitherto unknown chloro-pentammine, thus completing a rounded-out series of ammonia compounds of platinum predicted by the coordination theory.

Chugayev's pupils, I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinsky, N. K. Pshenitsyn, and others, greatly extended the further study of the chemistry of platinum metals. Lebedinsky synthesized the hitherto unknown mono-, di-, tri-, and tetraammines of trivalent rhodium, and also rhodium compounds with thiourea. I. I. Chernyaev was the first to obtain the cis-isomer of Gro platinum salt $[Pt(NH_3)_4Cl_2]X_2$, which was likewise confirmation of the deductions of the coordination theory. He also synthesized a series of optically active platinum complexes. Grinberg obtained the second isomer of diammine of palladium and new derivatives of monoammines of palladium. V. I. Goremykin described palladium compounds that contain hydrazine and hydroxylamine. New compounds of iridium, in particular, with urea, were synthesized. O. E. Zvyagintsev and his colleagues obtained nitroso-nitrates of divalent ruthenium. It was demonstrated that ruthenium is not precipitated from these substances under the action of various reagents that readily precipitate it in the case of other compounds. These properties are of great interest in accounting for the fact that radioactive isotopes of ruthenium are found to be very difficult to separate from nitric acid solutions obtained in the processing of neutron-irradiated uranium.

Complex compounds of platinum with organic addenda, ethylene, acetylene, were separated by A. D. Gelman. Together with L. N. Essen she synthesized for the first time a tetravalent platinum complex with six different innersphere addenda:

$$[Pt(C_5H_5N)\ (NH_3)\ (Cl)\ (Br)\ (I)\ (NO_2)]$$

In 1926, I. I. Chernyaev discovered the regularity of the "transeffect", which is the most important theoretical generalization in the chemistry of complex compounds during the past fifty years. He established that in complex compounds constructed according to the square or octahedron type, the strength of the bond of the given addendum with central atom depends on the nature of the addendum in the transposition. This affects reactions of its substitution by other atoms or molecules that are less amenable to the transeffect. For compounds of divalent platinum, a number of addenda arranged according to diminishing transactivity are of the following form:

$$CS(NH_2)_2 > N\overline{O}_2 > SC\overline{N} > Br^- > C\overline{l} > \frac{En}{2} > NH_3 > H_2O$$

(En - ethylendiamine). A still stronger transeffect than that of thiourea is exerted by ethylene, propylene, acetylene, nitric oxide, carbonic oxide, and certain other addenda.

The regularity of the transeffect permits foreseeing the trend of reactions in the internal sphere of coordinational structures. For this reason, it played an outstanding part in the development of syntheses of new complex compounds. The transeffect regularity that was discovered on compounds of divalent platinum was subsequently utilized with success for compounds of tetravalent platinum (here, the diminishing series of transactivity of the addenda is somewhat different), divalent palladium, trivalent rhodium, iridium, and cobalt, and also of certain other elements.

A. A. Grinberg and F. M. Filinov were the first to apply the method of isotopic exchange with the use of radioactive indicators for studying the relative mobility of addenda of the internal sphere in complexes of platinum and iridium. A. A. Grinberg and his colleagues carried out broad investigations into acid-base and oxidation-reduction properties of complex compounds of platinum metals, thus making it possible to find, for some of them, new practical applications, and also to expand theoretical knowledge about the nature of the bonds of internal-sphere addenda.

Hundreds of new compounds of platinum metals have been obtained and novel ways of synthesizing them have been worked out as a result of these investigations. The development of the chemistry of platinum metals has permitted the proposal of refined methods for separating and purifying these elements. Resulting from the development of this work is the creation, in the U.S.S.R., of one of the biggest schools in the chemistry of complex compounds and of a team of outstanding specialists in the technology and refining of platinum metals.

Prior to the Socialist Revolution of 1917, Russia mined considerable quantities of raw platinum, but there was no industrial refining of platinum and its associated minerals. On the basis of the works of the scientific school of Chugaev-Chernyaev, the Soviet Union has built up a platinum industry which produces from the country's raw material all platinum metals, and to a high degree of purity.

In the early 1920's, the young Soviet Republic was confronted with the problem of developing its own production of rare metals needed in the electric-lamp, radio, and ferro-alloy industries. In 1922, the laboratory of inorganic chemistry of the Moscow University began research into the chemistry and technology of tungsten, and molybdenum (T. M. Serbin, G. A. Meerson, V. I. Spitsyn, and others). A few years later they culminated in the organization of the production of tungsten and molybdenum wire for the electric lamp industry. The establishment of facilities for the production of refractory rare metals made it possible, later, to develop the output of hard alloys on the basis of tungsten carbide and to manufacture other compounds of this element. G. A. Meerson, I. A. Shlygina and others worked on problems associated with the technology of the production of the metals niobium and tantalum. At the same time, large-scale research into the chemistry of these elements was in progress. V. I. Spitsyn and his coworkers studied the structure of molybdates and tungstates of different elements, the conditions of formation of tungsten bronzes, the role of water in the structure of aquapoly compounds, and the mechanism of formation of anions of the heteropoly acids of molybdenum and tungsten. Wide use has been made in recent years of tracer techniques with the use of radioactive and stable isotopes. A new coordinational interpretation has been proposed for the structures of aquapoly and heteropoly compounds on the basis of oxonium groups and hydrogen bonds, taking electroneutral molecules of the appropriate acids or their anhydrides - H_2MoO_4, MoO_3, H_2WO_4, WO_3 - as the addenda of the internal sphere.

A. V. Lapitzky has published a series of researches into the chemistry of niobates and tantalates. For one thing, he has made a detailed study of the processes of dehydration and thermal stability of these compounds as a function of the nature of the cations that enter into their composition.

A large volume of work has been carried out by Soviet researchers in the chemistry of beryllium. Under the leadership of V. I. Spitsyn and G. F. Silina, studies have been made of methods of obtaining metallic beryllium and its compounds from Soviet raw material, and in 1933 production of beryllium was organized. A. V. Novoselova and her coworkers have synthesized a whole series of new complex beryllium fluorides and established the physico-chemical conditions of their formation and the structure and crystallo-chemical properties. New information has been obtained on the structural and chemical analogies between fluoro-beryllates and the sulphates of alkali and alkaline-earth elements. Complex compounds of beryllium oxyacetate with ammonia and the simpler aliphatic amines have been isolated. In structure, they proved to be close to "inclusion compounds".

The limits of this survey do not permit me to dwell in detail on the results of research carried out in the U.S.S.R. in the chemistry and chemical technology of lithium, rubidium and cesium, boron, gallium, indium and thallium, the lanthanides, germanium and many other rare metals. Suffice it to point out that these investigations were carried out on a large scale, yielding much new scientific material and at the same time making it possible to supply the Soviet Union with all the rare elements that are of practical or theoretical interest.

Soviet scientists have worked on other interesting chapters of inorganic chemistry. P. P. Budnikov has made a large contribution to the study of the chemistry of cements and proposed new types of inorganic binding materials. I. V. Tananaev and coworkers have investigated in detail the ferrocyanides of many elements and have established certain general regularities of their formation. Ya. A. Fialkov has made a study of coordinational compounds, the central atom of which is non-metallic in character - polyhalides, polysulphides, double halides of phosphorus, antimony and other elements, the derivative halides of iodine with organic substances, etc. G. G. Urazov and I. S. Morozov have made a broad study of the reaction of chlorination of oxides, sulphides and other compounds, and they have given a theoretical explanation of the processing of certain ores by this method. I. A. Kazarnovsky has obtained fresh data on the composition and structure of peroxide compounds of alkali elements. A. F. Kapustinsky developed the energetics of chemical reactions as a function of the position of the elements in the periodic table; K. B. Yatsimirsky developed the thermochemistry and crystallochemical energetics of complex compounds.

Traditionally, Soviet chemical investigations continue to deal with the periodic table of Mendeleyev and to develop its applications. We may give several instances that characterize the results of recent years.

A. E. Fersman showed that the periodic law governs, profoundly and comprehensively, the combination, distribution, migration and concentration of chemical elements in nature. He divided the Mendeleyev table into a series of geochemical fields that correspond to definite geochemical processes and associations of elements. Thus, the composition of minerals that are segregated at different stages of crystallization of silicate magma is closely bound up with the periodic law.

A. P. Vinogradov has studied the regularities of distribution of chemical elements in the upper part of the earth's crust, in particular, in the soil.

A. F. Kapustinsky has shown that the absolute entropies of free elements in the solid state under standard conditions (and also the entropies of ions in aqueous solutions) are a periodic function of the atomic numbers of the elements. Maxima correspond to the beginnings of the periods, that is, to the entropies of the alkali metals. Thus, thermodynamics has come to be linked up with the periodic law.

B. V. Nekrasov developed the concept of electron analogues, which concept theoretically substantiates the regularity of the ordinary (short) form of the periodic system and reveals the nature of the interconnection between subgroups of elements within large periods and the typical elements of each group.

N. V. Ageev and others have worked on applications of the periodic law to problems of the chemistry of metals and metallic alloys.

V. F. Zhuravlev has established that in cements the binding properties of a number of chemical compounds (silicates, aluminates, ferrites, and others) depend upon the position in the periodic system of elements forming the basic oxide in these substances.

A. A. Litvakovsky considered the periodicity of the melting temperatures of metals and the higher oxides of elements of the side subgroups of the periodic system and demonstrated that it may be connected with the formation of hybrid orbits during the accumulation, in the outer layer of the electron shell of the atom, of s- and d-electrons from 4 to 10 in the case of free elements, and from 2 to 4 in the case of ions that make up the oxides. The melting temperature maxima in the transition metals of the sixth group, and also of the higher oxides of the transition elements of the fourth group is indicative, apparently, of the fact that in both cases there is formed a maximum possible number of hybrid linking orbits for a given series. This theoretical reasoning permitted the above author to select a composition for a new refractory material that has proved more stable than earlier used kinds.

The activity of catalysts depends on the position of the component elements in the periodic system and on the chemical properties of the compound used. Using the case of the reaction of decomposition of hydrogen peroxide, G. M. Zhabrova, S. Z. Roginsky, and E. A. Fokina have shown that catalysts containing transition elements of large periods and possessing intense coloration, are, as a rule, considerably more active than uncoloured compounds that do not contain transition elements. A similar regularity was observed earlier for reactions of thorough oxidation of hydrocarbons.

N. N. Kavtaradze has detected a periodic dependence in the chemisorption ability of metals with respect to hydrogen and ethylene: elements of the first halves of periods of the system exhibit the phenomena of chemisorption, while elements of the second halves do not.

Radioactive elements have come to occupy a prominent place in modern science and technology. In pre-revolutionary Russia, research into these elements was on a small scale and was hampered by a lack of our own preparations of radium. However, Russian workers were clearly aware of the importance of investigations into the phenomena of radioactivity. In 1910, V. I. Vernadsky wrote: "The phenomena of radioactivity now open up before us sources of atomic energy that exceed millions of times over all those sources of power that have ever been visualized by human imagination, in comparison with which the power of steam, of electricity and of chemical explosives fades to insignificance. Humanity is entering a new age of radiant atomic energy."

The development of a method of extracting radium from our own uranium-vanadium ores was the first assignment of the Soviet Government to the Academy of Sciences in 1918. This assignment was completed successfully. In 1921, an experimental radium plant supervised by V. G. Khlopin produced the first preparation of Soviet radium. Several years later, the same raw material was used to organize the production of pure compounds of uranium.

Research into the chemistry of radioactive elements was first concentrated in the Radium Institute of the Academy of

Sciences, and then was expanded in other research institutes and laboratories. The principal trend in the works of V. G. Khlopin and his pupils (I. E. Starik, B. A. Nikitin, A. E. Polesitsky, A. P. Ratner and others) was the study of the laws of coprecipitation of radioactive elements, in the state of extremely diluted solutions, with crystalline or amorphous sediments precipitated from solutions. The foregoing phenomena made it possible to elucidate the mechanism of the process of fractional crystallization (the most important method, at the time, of concentrating radioelements) and later were of exceptional significance in analytical chemistry. Established was the important role of isomorphism of the precipitating sediment and the compound formed by the radioelement present in the solution. A quantitative study of the process of fractional crystallization on the basis of industrial experience and extensive laboratory investigations led Khlopin, in 1924, to the discovery of the following law: <u>a microcomponent that yields an isomorphous compound in the solid phase is distributed between the crystals and the solution as a dissolved substance between two solvents that do not mix</u>.

The following equation was proposed for a quantitative evaluation of the distribution of radium between crystals of barium salt and the solution:

$$\frac{x}{m} = K\frac{1-x}{v},$$

where x is the quantity of radium that has passed into the crystals, m is the weight of the solid phase, 1-x is the quantity of radium remaining in solution, v is the volume of the solution, K is a constant characteristic of each pair of salts.

If by x and 1-x we designate, respectively, the quantity of microcomponent that has passed into the crystals and that which remains in solution, and by y and 1-y the quantity of macrocomponent that has passed into the crystals and that which remains in solution, then the process of fractional crystallization is characterized by the following relations:

$$\frac{x}{y} \Big/ \frac{1-x}{1-y} = D ,$$

where D is the fractionation factor.

A study of over 30 systems containing (as microcomponents) radium, polonium, radium D (Pb^{210}) and other radioactive elements, has shown them to obey strictly the law of distribution. The part of macrocomponents was played by the salts of barium, lead, uranium, cerium, and other elements.

The Soviet radium industry has made wide use of the practical conclusions from the scientific work of Khlopin's school. Considerable refinements were introduced into the separation techniques of radium and barium. In addition, these scientific investigations made it possible to train a considerable number of radiochemists who subsequently provided the scientific supervision and practical operation of radiochemical production in the Soviet atomic industry.

Methods of isomorphous cocrystallization with the use of radioactive indicators were used by V. G. Khlopin and B. A. Nikitin for studies of the phenomenon of second-order isomorphism, when isomorphic substitution occurs in the case of the same chemical type of structure of the substances, but independently of their chemical analogy ($BaSO_4$-$KMnO_4$, $KClO_4$-KBF_4, NaBr-PbS etc.). Utilizing the systems $KClO_4$-$Pb^{210}SO_4$, $RbClO_4$-$RaSO_4$ and others, they showed that with concentrations of the order of 10^{-6} per cent, lead and radium do not enter into the crystal lattice of perchlorates. Consequently, second-order isomorphous substitutions have a lower limit of mixability. At the same time, the perchlorates that were studied could capture the sulphate of radium or lead if the latter were in concentrations sufficient for the construction of their own crystal lattice. Thus, in the case of true isomorphism, substitution occurs ion by ion, atom by atom or molecule by molecule; but in the case of second-order isomorphism, the suggestion was made that substitution takes place by entire sections of the crystal lattice from the size of one elementary cell to a comparatively large number of them.

The use of radioactive indicators has opened up new paths for studying the phenomena of isomorphism. For example, this technique has made it possible, in several cases, to establish the existence of nonstable compounds or those present in negligibly small quantities, for example, 2- and 6-valent polonium, to study their composition and structure. Application of the method of isomorphous coprecipitation to systems containing gaseous substances enabled Nikitin, for the first time, to prove the existence of the chemical compounds of radon and other inert gases with water, toluene and phenol.

In the Soviet Union, broad studies have been made of the chemistry of the most important radioactive elements -

uranium and thorium. A. A. Grinberg and co-workers have demonstrated that the oxalate of tetravalent uranium $U(C_2O_4)_2.6H_2O$ exhibits acidic properties due to dissociation according to the following scheme:

$$\left[U(C_2O_4)_2(H_2O)_n\right] \rightleftharpoons \left[U(C_2O_4)_2(H_2O)_{n-1}OH\right] + H^+.$$

Similar behaviour is exhibited by uranyl oxalate $UO_2C_2O_4.3H_2O$. Thorium oxalate, $Th(C_2O_4)_2.6H_2O$, practically does not display any acidic properties at all.

I. I. Chernyaev and his collaborators have synthesized a number of new oxalate complexes of uranium and worked out a method of obtaining aqueous and anhydrous uranyl carbonate. V. I. Spitsyn, E. A. Ippolitova and others have studied the properties of the uranates of alkali elements. It was established that the thermal stability of these compounds increases when passing from lithium uranate to cesium uranate. However, the greatest heat of formation is found for the uranates of potassium and rubidium. A thermographic and roentgenophase investigation of the process of interaction of alkali carbonates with uranium oxides has shown that in the first stage of the reaction there are formed, at a temperature of about 500°C, ordinary diuranates, which subsequently, depending upon the excess of one of the reagents convert to normal uranates or to more acid poly-uranates. Basic uranates of composition Me_4UO_5 have been obtained.

A number of authors have studied the composition and properties of peruranates. S. A. Shchukarev and his co-workers have investigated the chlorides and oxychlorides of uranium. A new oxychloride of trivalent uranium -- UOCl -- has been obtained. A study has been made of the process of reduction of thorium halides by means of hydrogen. The properties of $ThCl_3$ and $ThBr_3$ have been described. Different workers have obtained many new complex compounds of uranium with organic substances -- 1,3-diketones, benzoyl acetone, Schiff's bases, etc. Of particular interest are studies of the products of interaction of uranyl nitrate with organic solvents (V. M. Vdovenko et al.).

Other naturally radioactive elements were likewise investigated. B. N. Laskorin developed a convenient method for the chromatographic separation of barium and radium. I. E. Starik and L. D. Sheidina proposed a method of coprecipitation of protactinium with zirconium mandelate as a good method for its radio-chemical purification and analytical determination. A. K. Lavrukhina and others have studied the extraction method of separating actinium from uranium ores and its determination by the daughter Fr^{223}.

The development, in the U.S.S.R., of the atomic industry and of acceleration techniques of elementary particles has made accessible the transuranium and fission elements, in which sphere much research has been done.

A. D. Gelman and her collaborators have studied the composition of oxalate complexes of trivalent plutonium, and by the method of ion exchange have determined the constants of their instability. By the spectrophotometric method, a study has been made of complex-forming in the system neptunyl-ion -- acetate-ion. A chemical method has been proposed for obtaining trivalent neptunium with the use of rongalite as the reducing agent. A study has been made of the stability of valence states of plutonium in solutions of nitrates. It has been shown that Pu(VI) in these conditions is stable; Pu(IV) disproportionates with the formation of Pu(III) and Pu(V), while Pu(V) disproportionates to Pu(IV) and Pu(VI). In addition, there are a number of side reactions. The degree of disproportionation of Pu(IV) increases with diminishing concentration of hydrogen ions; for Pu(V) the picture is the reverse. Also studied by ion-exchange methods were the composition and dissociation constants of complexes of ethylenediaminetetraacetic acid with Pu(III), Pu(V), Am(III), and Am(V).

A method has been worked out for the separation of americium from fission waste solutions containing a fraction of rare-earth elements (G. N. Yakovlev et al.). For this purpose, use is made of coprecipitation of americium with potassium uranyltricarbonate, $K_4[UO_2(CO_3)_3]$. Americium is first oxidized to the pentavalent state. A study has been made of the process of disproportionation of Am(V), which takes place according to the scheme: $3AmO_2^+ + 4H^+ \rightleftharpoons 2Am_2^{2+} + Am^{3+} + 2H_2O$. A spectrophotometric investigation of the behavior of americium ions in solutions made it possible to detect the self-reduction of Am(V) to Am(III) by the products of decomposition of water under the action of americium radiation. Similarly, Am(VI) reduces to Am(V).

P. I. Artiukhin and others have studied the self-reduction of plutonium (VI) in solutions and have attributed this phenomenon to a reaction with hydrogen peroxide that forms under the action of α-radiation on water. V. V. Fomin and others have shown that as a result of the storage of oxalates of Pu(III), Pu(IV) and Pu(VI), these compounds decompose under the action of the α-radiation of plutonium, at the expense of the carbonic oxide that forms. In this process, the oxalates are converted into carbonates and, partially, into oxides.

Research has also been conducted in the U.S.S.R. on the far-transplutonium elements. A group of Soviet workers (L. I. Guseva, K. V. Filippova et al.) have carried out experiments to obtain isotopes of einsteinium and fermium by bombarding a uranium target with nuclei of nitrogen and oxygen on a cyclotron with pole diameter of 150 cm. The transplutonium elements obtained were separated by chromatography. At the same time, isotopes of californium, berkelium and curium were identified.

In 1957, G. N. Flerov, S. M. Polikanov and others irradiated plutonium-241 with an intense flux of quintuply-charged O^{16} ions and detected (by means of photographic plates) alpha particles of energy 8-9 Mev, which may be attributed to element No. 102.

A large number of studies have been carried out in the U.S.S.R. in the chemistry of uranium fission products. N. E. Brezhneva and coworkers have developed a composite method of separating the fission elements from waste solutions of radiochemical production. Among the radioisotopes, cesium-137 has attracted the attention of Soviet workers. B. A. Zaitsev, A. I. Grivkova, E. I. Malinina, and others have worked out a method of manufacturing highly active sources of it. Cesium-137 is extracted from the mixture of fission elements on a residue of nickel-potassium ferrocyanide. The concentrate obtained is subjected to an alternate series of acid and alkali treatment. The insoluble residue is calcinated after which the cesium is almost completely dissolved out by water. The cesium is then transferred to the chloride form, which, if necessary, is passed through a supplementary chemical purification. This method has made it possible to obtain preparations of cesium-137 with specific activity 20 curies per gram and 99.9 per cent radiochemical purity.

V. I. Spitsyn and A. F. Kuzina have worked out a convenient method of separating technetium-99 from neutron-irradiated molybdenum anhydride and obtained milligram quantities of this element in a radiochemically pure form. To separate it from molybdenum, use was made of sorption of technetium in an ammonia medium on a precipitate of magnesium phosphate. Final purification was carried out by the chromatographic method.

Radiochemical investigations have played an important part in the study of processes of the distribution of atomic nuclei under the action of high-energy elementary particles. Special methods of radiochemical analysis were elaborated for purposes of separating and identifying the radioactive isotopes that form.

A. P. Vinogradov and his coworkers (I. P. Alimarin, V. I. Baranov, A. K. Lavrukhina, et al.) have made an extensive study of the nature of the fission products of copper, silver, bismuth, and several other elements resulting from fast particles - protons and deuterons of energy 100 to 700 Mev. Through the use of precision techniques of radiochemical analysis, several tens of new radioactive isotopes have been discovered, and the yields of separate isotopes in various nuclear transformations (fission, splitting, the ejection of light nuclei, etc.) have been computed. For example, the yields of 240 isotopes (mainly from Sr^{89} to Eu^{154}) have been determined under the irradiation of uranium with protons of energy 480 Mev. In the case of thorium, 244 isotopes (from Se^{83} to Eu^{152}) have been detected, and 252 for bismuth (from Ga^{72} to Ba^{129}). The yield curves of various isobars distributed according to their ordinal numbers are dome-shaped. Their width is 2 to 3 units of the ordinal number. Characteristic of nuclear fission by high-energy particles is the constant distribution of charge irrespective of the mass number of the fission fragments and the element number of the fissioning nuclei. On the basis of these studies, an explanation has been found for the fission mechanism of uranium and thorium nuclei under the action of high-energy particles. Apparently, it is of a mixed nature: the excited nucleus evaporates a certain number of neutrons after which the fission process sets in. In turn, the excited fragments that form, evaporate neutrons.

Organic chemistry in the U.S.S.R. has made a large progress. At the time of the October 1917 Revolution our country had such prominent leaders in chemistry as N. D. Zelinsky, A. E. Favorsky, A. E. Chichibabin. With immeasurably better conditions for scientific research, they greatly expanded their investigations and created big schools of pupils.

Characteristic of the Moscow school of organic chemists of N. D. Zelinsky is a broad study of various classes of hydrocarbons and their catalytic-transformations. These investigations led to a complete change in the views of the reaction ability of aliphatic, alicyclic and aromatic hydrocarbons. The discovery of processes of their mutual transformability with definite catalysts and under appropriate temperature conditions ensured the industry of organic synthesis with raw materials, one way being the transfer of aliphatic and alicyclic hydrocarbons into more valuable unsaturated aromatic hydrocarbons. On the other hand, the accumulation of extensive experimental material created favourable conditions for broad theoretical generalizations in the field of organic catalysis, which found expression in the creation of the multiplet theory (A. A. Balandin). At the same time, many new hydrocarbons were obtained and studies made of their physico-chemical properties. The petroleums of various parts of the U.S.S.R. were subjected to a broad chemical investigation. Methods of purifying and refining oil and its products were studied and improved (N. D. Zelinsky, S. S. Nametkin, et al.).

One can give only a brief review of the most important types of catalytic transformations of hydrocarbons that were discovered by N. D. Zelinsky and his pupils.

The dehydrogenation catalysis of alicyclic hydrocarbons has yielded especially valuable results. The catalysts were platinum or palladium deposited on activated carbon, or nickel on aluminium oxide. At specific temperatures (300°C) the reactions are complete, for example, cyclohexane converts into benzene. Similar behavior is exhibited by the homologues of cyclohexane and decahydronaphthalene (N. D. Zelinsky, N. I. Shuikin, Yu. K. Yuriev, and others). This process proceeds most readily with six-member cyclic hydrocarbons. Under more stringent conditions, cyclopentane hydrocarbons can also undergo aromatization. Given a mixture of hydrocarbons, there is observed a selective dehydrogenation of cyclohexane hydrocarbons, while the others remain unchanged. The application of dehydrogenated catalysis to naphthene hydrocarbons of petroleum with the object of their aromatization has found an important technical use (N. D. Zelinsky, N. I. Shuikin, S. S. Novikov). The process of catalytic processing of petroleum fractions into motor fuel -- platforming -- is actually based on conclusions from the work of Zelinsky and his coworkers.

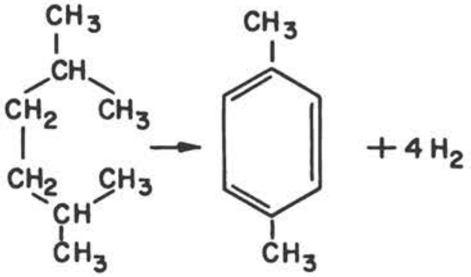
At temperatures of 500 to 600°C, saturated hydrocarbons on oxide catalysts convert into olefines and further into diolefines (N. D. Zelinsky, A. A. Balandin, O. K. Bogdanova, et al.). For example, butane turns into butylene and further into butadiene:

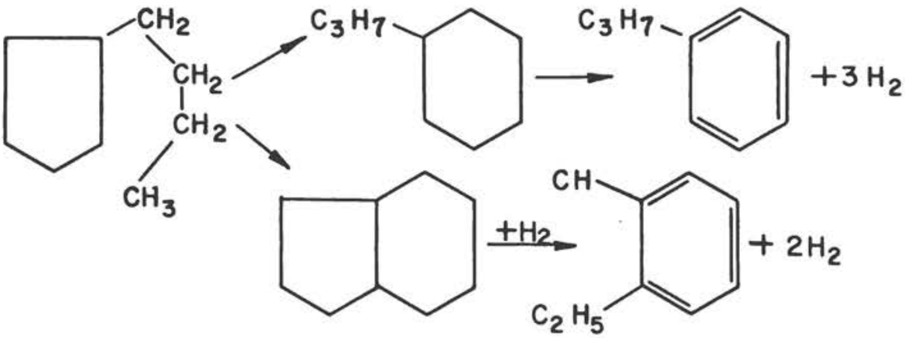
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2 = CH\text{-}CH_2\text{-}CH_3 + H_2$$

$$CH_2 = CH\text{-}CH_2\text{-}CH_3 \longrightarrow CH_2 = CH\text{-}CH = CH_2 + H_2 .$$

Similarly, ethylbenzene converts into styrene.

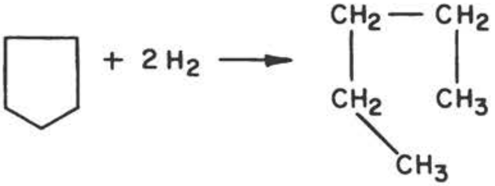
Aliphatic hydrocarbons containing at least six atoms of carbon in the chain, and also alkylcyclopentanes are subjected to dehydrogenation on platinized carbon or on oxide catalysts with the formation of aromatic hydrocarbons (B. A. Kazansky, A. F. Plate, B. L. Moldavsky, et al.):





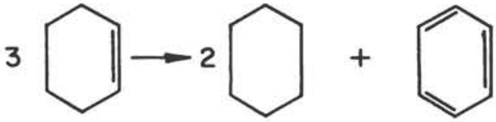
At 310°C on a platinum catalyst there takes place cyclization of hydrocarbons of the aliphatic series into alicyclic (B. A. Kazansky, A. L. Liberman, et al.), for example, 2,2,4-trimethylpentane is transformed into 1,1,3-trimethylcyclopentane while n-heptane is converted into 1,2-dimethylcyclopentane and ethylcyclopentane.

The reverse process, too, has been established: the conversion of alicycles into saturated hydrocarbons of the aliphatic series (N. D. Zelinsky, B. A. Kazansky, and A. F. Plate). For instance, cyclopentanes in the presence of platinized carbon at 290° are converted into n-pentane:



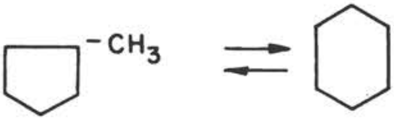
Cyclopropane and cyclobutane are more easily hydrogenated than cyclopentane.

Of considerable interest is the so-called irreversible catalysis in which unsaturated alicyclic hydrocarbons disproportionate converting into a mixture of saturated alicyclic and aromatic hydrocarbons (N. D. Zelinsky, B. A. Kazansky, R. Ya. Levina, and others). For example, cyclohexene at room temperature, in the presence of platinum or palladium, is converted to cyclohexane and benzene:



Various unsaturated hydrocarbons with six-member cycles, including mono- and bicyclic terpenes enter into this reaction.

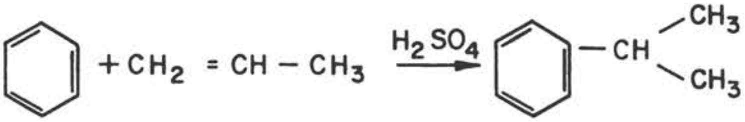
A series of studies has been devoted to isomeric transformations of cyclic hydrocarbons. The transformation of cis-dekaline into trans-dekaline, and cis-hydrindane into trans-hydrindane in the presence of anhydrous $AlCl_3$ or $AlBr_3$ proceeds readily (N. D. Zelinsky, M. B. Turova-Polyak). At low temperature (not over 100°C), the homologues of cyclopentane convert into the homologues of cyclohexane, while at higher temperatures, the reverse process takes place. For example, methylcyclopentane turns into cyclohexane, and there is formed an equilibrium mixture of both hydrocarbons (with a predominance of the second):



The other homologues of cyclopentane convert to a mixture of methylated cyclohexanes, cycloheptane into methylcyclohexane, etc.

There is also observed isomerization of normal aliphatic hydrocarbons with transition into hydrocarbons with branched chains (A. D. Petrov). R. Ya. Levina has described the catalytic isomerization of unsaturated hydrocarbons accompanied by transposition of the multiple bond and alteration of the chain structure. For example, octene-I is converted into a mixture of isomeric methylheptenes (the catalyst is beryllia).

Of extreme technical significance is the extensive research, carried out in the U.S.S.R., of reactions of alkylation of hydrocarbons. A. V. Topchiev, Yu. G. Mamedaliev, K. P. Lavrovsky and others have studied the alkylation by olefines of aromatic and saturated aliphatic hydrocarbons. It proved possible to obtain the higher homologues of benzene by means of alkylating benzene with olefines under slight pressures in the presence of sulphuric acid, for instance:



Catalysts in such reactions are $AlCl_3$, various aluminosilicates and natural clays, and also boron trifluoride and its complex compounds. On the basis of these processes, the production of certain types of motor fuel and valuable semiproducts for the chemical industry was organized.

The catalytic alkylation of isoparaffines by olefines is likewise of great practical importance. This was done for the first time by V. N. Ipatiev using $AlCl_3$ as catalyst. Boron trichloride and its complexes were more convenient and did not cause side reactions. The mechanism of these reactions has been studied in detail by A. V. Topchiev and his coworkers.

A large group of investigations was carried out in connection with the problem of cracking of hydrocarbons. As early as the mid-19th century, the thermal processing of petroleum was studied vigorously in Russia. The basic principles of modern thermal cracking were elaborated by V. G. Shukhov in 1890. However, they found their first application in production only much later and in the U.S.A. The idea of catalytic cracking underlay the early works of N. D. Zelinsky, who in 1918 used aluminum chloride as catalyst for the destruction of heavy hydrocarbons: during the civil war there was the problem of converting into gasoline, the reserves of solar oils which were then available in the central regions of Soviet Russia. Beginning with the first five-year plan, the production of cracking gasoline began to play an important role in the national economy of the U.S.S.R. In the theory and mechanism of reactions of thermal and catalytic cracking, valuable results were obtained by A. V. Frost, A. I. Dintses, V. V. Voevodsky, and others, who regarded the pyrolysis of hydrocarbons as a chain radical process. A new high-speed method of catalytic cracking of oil was developed by K. P. Lavrovsky.

Soviet workers extensively developed methods of synthesis of individual hydrocarbons for a comprehensive study of their properties and technical characteristics (B. A. Kazansky, A. D. Petrov, and others.).

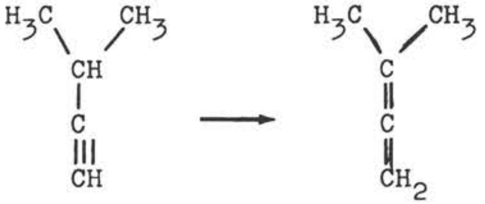
A number of investigations were carried out with respect to the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen (N. D. Zelinsky, B. A. Kazansky, Ya. T. Eidus, et al.). It was found that methylene radicals originated in the interaction of carbon monoxide and hydrogen. Their subsequent polyrecombination leads to the formation of a hydrocarbon chain:

$$CO + H_2 \longrightarrow H\text{-}\underset{\cdot}{C}\text{-}OH \xrightarrow[-H_2O]{H_2} \dot{\underset{\cdot}{C}}H_2$$

$$n\dot{\underset{\cdot}{C}}H_2 \longrightarrow C_nH_{2n}$$

$$C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2}\ .$$

A great contribution to the chemistry of acetylene and diene hydrocarbons has been made by the Leningrad school of A. E. Favorsky and his pupils. The studies of this school began during the pre-revolutionary period when Favorsky discovered the acetylene-allene and allene-diene regroupings of the hydrocarbon series C_nH_{2n-2} under the action of alcoholic alkali. Subsequent investigations led to the establishment of general regularities of such regroupings, which proved to be typical allyl (α, γ)-transpositions, for example, for isopropylacetylene



In a number of cases, more complex regroupings occur with subsequent migration of a double or triple bond.

A. E. Favorsky likewise discovered a new type of isomerization which allows for the transformation of chlorated ketones into acids of the acryl series. It is known that these unsaturated acids now play a highly important role in the production of organic glass and synthetic rubbers. Favorsky's discovery, over 50 years ago, of the reaction of the union of alcohols to acetylene served as a method for obtaining various simple vinyl ethers that now serve as the initial raw material for a synthesis of polymer materials.

After the October revolution of 1917, Favorsky threw himself with great energy into problems of the synthesis of rubber, and proposed a simpler method of obtaining isoprene from acetone and acetylene than had been accomplished in other countries (incidentally, also on the basis of reactions that had already been described by Favorsky). There is a big future open to isoprene rubber when the production of acetylene becomes cheaper. Favorsky also introduced essential refinements in the method of obtaining chloroisoprene rubber.

The reaction, discovered by Favorsky, of the formation of acetylene alcohols through the interaction of acetylene, phenylacetylene and ketones in the presence of potassium hydroxide, was brilliantly developed in the works of I. N. Nazarov. As a result of a broad development of syntheses on the basis of vinylacetylene and various ketones, Nazarov prepared a large number of new and valuable organic compounds.

A. E. Favorsky and M. F. Shostakovsky worked out simplified methods of the synthesis of vinyl esters, making it possible to put them into production.

An outstanding role in the Soviet research into synthetic rubber was played by S. V. Lebedev, one of Favorsky's pupils. Before the 1917 October Revolution, Lebedev had studied the processes of polymerization of diolefines in the case of divinyl, isoprene and di-isopropenyl. At the same time, he obtained rubber-like polymers of these substances. After the Revolution, Lebedev paid special attention to developing methods of obtaining butadiene (from alcohol) and its polymerization into rubber. Prior to Lebedev's work, butadiene was obtained (according to I. I. Ostromyslensky) in two stages: first the alcohol was dehydrogenated into acetaldehyde

$$C_2H_5OH \longrightarrow CH_3COH + H_2 \quad ,$$

and then, in the joint dehydration of alcohol and aldehyde, divinyl was obtained:

$$C_2H_5OH + CH_3COH \longrightarrow CH_2 = CH\text{-}CH = CH_2 + 2H_2O \ .$$

In 1926-28, Lebedev developed a remarkable single-stage process based on a mixed dehydrogenating and dehydrating catalyst:

$$2\ C_2H_5OH \longrightarrow CH_2 = CH\text{-}CH = CH_2 + 2H_2O + H_2 \ .$$

At the same time Lebedev worked out a method of polymerization of divinyl into rubber with the aid of metallic sodium. In 1930, an experimental plant was built on the basis of Lebedev's method, and in 1932 the U.S.S.R. began industrial production of sodium-butadiene rubber, which assumed tremendous proportions and supplied all the needs of the national economy.

Lebedev's pupils and coworkers continued refining the process that he had developed. In the Soviet Union, it is still the main process for the production of synthetic rubber, although we have recently organized the production of other elastic materials ("cold" and "hot" copolymers of butadiene with alcohol, methylstyrene and other products; polyisoprene, chloroprene, polysiloxane rubbers, and others). At present the Soviet Union produces over 20 types of synthetic rubber.

One of the most important trends of Soviet organic chemistry is the chemistry of organo-element compounds, in the development of which particular merit goes to the school of A. N. Nesmeyanov.

Organo-element compounds were studied by Russian chemists prior to the October Revolution. Thus, at the end of last century, A. M. Butlerov and A. M. Zaitsev applied organometallic compounds in organic synthesis. Organo-magnesium compounds were investigated by V. V. Chelintsev. P. P. Shorygin discovered interesting reactions of metallizing, while A. E. Arbuzov was one of the originators of the organic chemistry of phosphorus. However, the chemistry of organo-element compounds saw broad development only in the 1930's and 1940's.

Research in the field of organo-metallic compounds during the Soviet period was begun by A. N. Nesmeyanov, K. A. Kocheshkov, G. A. Razuvaev, and V. N. Ipatiev (1927-1932). Later, work was done in this field by R. Kh. Freidlina, O. A. Reutov, I. F. Lutsenko, A. E. Borisov, N. K. Kochetkov, and others. The chemistry of organo-phosphorus compounds was studied by the school of A. E. Arbuzov and B. A. Arbuzov, and also by M. I. Kabachnik and his pupils. Organo-silicon compounds were studied by B. N. Dolgov and K. A. Andrianov, the chemistry of silicon-hydrocarbons was studied by A. D. Petrov, the chemistry of the organic compounds of fluorine by I. L. Knunyants.

The development of organo-element chemistry in the U.S.S.R. proceeded in the direction of studies of possible structures and properties of compounds corresponding to these structures, the development of new methods of synthesis, and ways of practical utilization of the new substances. Investigated were the organic compounds of many elements: Li, Na, Mg, Zn, Cd, Hg, B, Al, Te, Si, Ti, Zr, Ge, Sn, Pb, Cr, P, As, Sb, Bi, Br, I, F, Fe, Pt.

Soviet chemists worked out diverse methods for the synthesis of organo-element compounds. In 1929, A. N. Nesmeyanov, utilizing the synthesis of organo-mercuric compounds, developed a method of double diazonium salts, which proved unusually valuable:

$$(ArN_2X)_m \cdot MeX_n + \frac{2m}{p} Me' \longrightarrow Ar_m MeX_{n-m} + \frac{m}{p} Me'X_n + N_2 .$$

This method was applied to the synthesis of organic derivatives of tin, lead, arsenic, antimony, bismuth, and thallium (in addition to mercury). A method, similar to this one, of double halide-onium salts was found by O. A. Reutov for compounds of mercury, tin, antimony and bismuth:

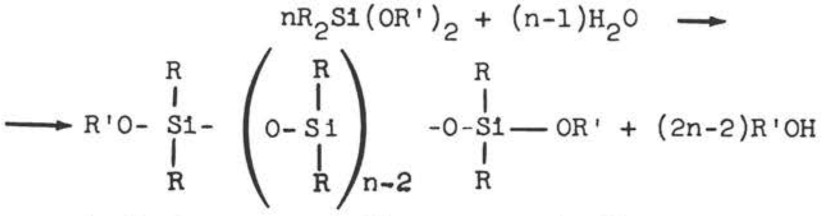
$$(Ar_2Hal\ Cl)\ Me\ Cl_n + \frac{2m}{p} \cdot Me' \longrightarrow Ar_m\ MeX_{n-m} + \frac{m}{p} Me'X_p .$$

Later, A. N. Nesmeyanov and his school worked out other methods of obtaining organo-element compounds: the synthesis of aromatic "onium" compounds by "transplantation" of arylcation, the hydrazone method, the method of attaching the halides of mercury and antimony to acetylene, and others.

G. A. Razuvaev and his coworkers studied the synthesis of organo-metallic compounds via radicals that are formed by peroxides (for example, in their decomposition or as a result of photochemical processes). Just recently, K. A. Kocheshkov and colleagues described an interesting method of obtaining organo-tin compounds via interaction between metallic tin and haloid alkyls under the action of the gamma radiation of cobalt-60. Soviet chemists have also worked out a number of ways of synthesizing organo-element compounds.

One of the chief ways of synthesizing organo-phosphorus compounds is the reaction of Arbuzov regrouping (regrouping of esters of phosphoric acid under the action of haloid alkyls), which was discovered by A. E. Arbuzov before the October Revolution. During Soviet times this method has been intensively developed. Other methods of synthesizing organo-phosphorus compounds, proposed by A. E. Arbuzov and his school, include the reaction of aldehydes and ketones with dialkylphosphites, the method of attaching dialkylphosphoric acids to unsaturated compounds, and others. A number of methods of synthesizing organo-phosphoric compounds were developed by M. I. Kabachnik and coworkers.

During recent years there has been a great development of synthetic methods in the field of organo-silicon compounds thanks to the discovery, by K. A. Andrianov in 1937, of polymer organo-siloxanes. Polymer chains consisting of -Si-O- links are formed in the incomplete hydrolysis of esters of silicon acids:



$$nR_2Si(OR')_2 + (n-1)H_2O \longrightarrow$$

$$\longrightarrow R'O-\overset{R}{\underset{R}{Si}}-\left(O-\overset{R}{\underset{R}{Si}}\right)_{n-2}-O-\overset{R}{\underset{R}{Si}}-OR' + (2n-2)R'OH$$

These products have found diverse application.

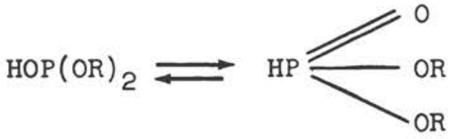
A. N. Nesmeyanov and his school have, during recent years, developed new synthetic methods in the field of derivatives of ferrocene.

Extensive investigations of Soviet chemists deal with the application of organo-magnesium and organo-lithium compounds in synthesis (A. P. Terentiev, A. N. Nesmeyanov, A. D. Petrov, A. E. Arbuzov, Yu. S. Zalkind, and others). K. A. Kocheshkov and his coworkers have for the first time worked out a method for obtaining individual organo-lithium compounds.

I. L. Knunyants and his collaborators have made a broad study of the chemistry of fluorolefins. They investigated reactions of attachment to them of nucleophylic and electrophylic agents. A study was made of the order in which alcohols and mercaptanes are attached to nonsymmetrical fluorolefines; vinyl substitution of fluorine atoms by alkoxyl has been established; allyl regroupings of perfluoro-allyl derivatives have been demonstrated; reactions of the nitration of fluorolefines were studied.

Organo-element compounds are widely used in the national economy of the U.S.S.R. To illustrate, let us take the large-scale production of antiknock substances -- tetraethyl lead, the production of organo-phosphorus flotation agents, the production of organo-mercuric fungicides and bactericides, the production of "teflon", polysiloxane resins, polysiloxane rubber and others. Of great practical interest are new methods of synthesizing triethylaluminum and tri-isobutylaluminum -- new catalysts of the polymerization of olefines, the discovery of new organo-phosphorus medical preparations "Armin", "Phosarbin" and others, the production of new highly effective organo-phosphorus insecticides, etc.

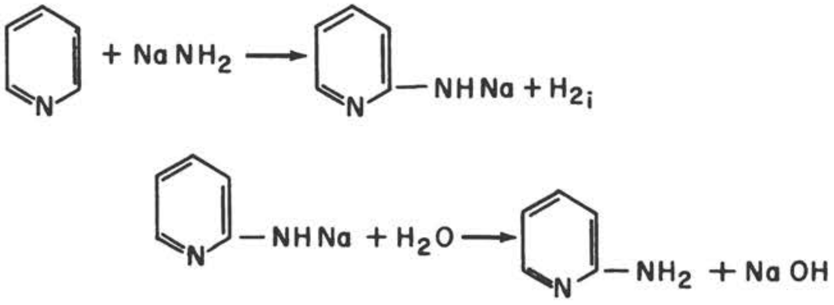
In the study of organo-element compounds, Soviet chemists have obtained a series of results of fundamental importance. A. E. Arbuzov discovered a new type of diade tautomerism of dialkyl-phosphites:



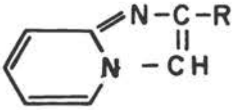
and found this phenomenon to be analogous to keto-enol tautomerism. On the basis of investigations into organo-metallic compounds, Nesmeyanov and his coworkers have conclusively demonstrated the possibility of a dual reaction capacity in the absence of tautomerism.

The investigations of A. E. Chichibabin in the field of heterocyclic compounds have been profoundly and systematically developed since the very first years of Soviet power.

In 1918, Chichibabin and O. A. Zeide discovered the reaction of amidation of pyridine, its homologues and analogues by the action of sodium amide (Chichibabin's reaction):



Utilizing this reaction, A. E. Chichibabin and his school (O. A. Zeide, A. V. Kirsanow, I. L. Knunyants, A. F. Egorov, N. N. Vorozhtsov, and many others) broadly developed the field of derivatives of pyridine, hinoline, pyrimidazol, and other heterocyclic compounds. Extremely interesting among these investigations are the following: the condensation of α-aminopyridine with β-chloroketones that has led to a new heterocyclic system of pyrimidazol



which correspond to the condensation of α-picoline, as a result of which a field of the derivatives of indolicine was discovered; catalytic methods of the synthesis of pyridine bases from aldehydes and ammonia; syntheses of oxy-derivatives of the pyridine and hinoline series, and others.

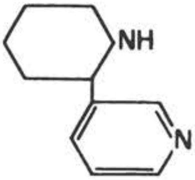
A. E. Chichibabin established a numerous school of chemists specializing in heterocyclic compounds. This laid a firm foundation for subsequent studies in the field of heterocyclic medicines. As a result of the work of I. L. Knunyants, G. V. Chelintsev, and O. Yu. Magidson on the synthesis of antimalarial substances, our industry is producing such preparations as achrihin. Of other similar studies, mention should be made of investigations by M. N. Shchukina into the production of "ftivazid",

which has found wide application in tuberculosis therapy. G. V. Chelintse and E. V. Benevolenskaya have worked out a simple method of synthesizing vitamin B_1.

The work of M. V. Rodionov in the chemistry of heterocyclic compounds has been extremely fruitful. He has developed elegant syntheses of glyoxalidones, pyrimidones and others, proceeding from β-amino acids. I. L. Knunyants and his coworkers have investigated methods of getting and converting in the row azlactones, β-lactames, oxazolones, etc. New and interesting methods of obtaining heterocyclic compounds (on the basis of β-chlorovinylketones) have been worked out by A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya. The chemistry of the derivatives of thiophene is being successfully developed by Ya. L. Goldfarb. A number of workers are studying synthesis on the basis of furfurole. Yu. K. Yuriev has worked out methods of the synthesis of selenophene and selenophane and their homologues and certain condensed heterocycles, and has also studied the mutual catalytic transformations of cycles with different hetero-atoms. The school of

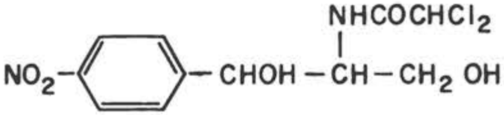
N. A. Demyanov has applied the Demyanov reaction (the action of nitrous acid on alicyclic amines) in the chemistry of heterocycles. This yielded very valuable results, for instance, α-aminomethylpyrrol was transformed into pyridine. A. P. Terentiev synthesized sulfo acids of the series of pyrrole, furan, indole, and others, using pyridinesulfotrioxide as the sulfurating agent.

The investigations of A. P. Orekhov and his pupils made for a considerable development of the chemistry of alkaloids. A systematic study was made of the alkaloid-bearing flora of the U.S.S.R., including about 800 plants within the country, and 50 new alkaloids were found. In the majority of cases it was possible to establish the structure of the alkaloids, which was, in a number of cases, corroborated by synthesis. Many of the discovered alkaloids have found practical application in medicine and are now being produced by the chemicopharmaceutical industry. Of greatest interest is the isolation, determination of structure, and synthesis of anabazine (α-pyperidyl-β-pyridine)

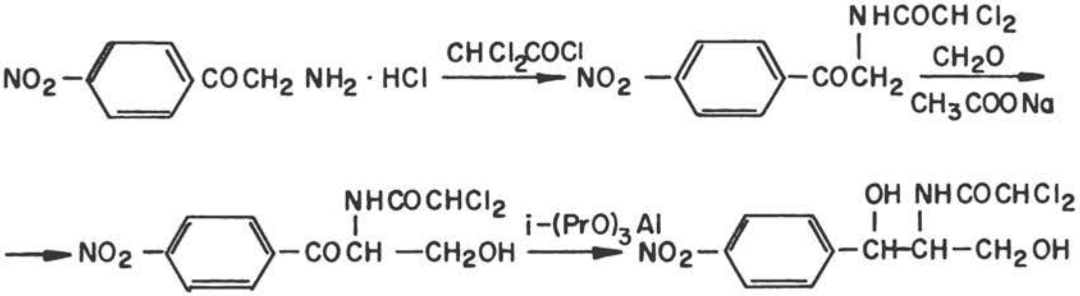


which possesses strong insecticide properties. At the present time, large-scale investigations in the chemistry of alkaloids are being carried out by S. Yu. Yunosov, and A. S. Sadykov (Uzbek SSR).

Attention should be drawn to the progress made by Soviet workers in the chemistry of antibiotics. M. M. Shemyakin and his coworkers have carried out important research in the field of levomycetine. Soviet researchers (simultaneously with the Americans) synthesized racemic levomycetine -- syntomycine:



The Soviet method proved simpler than the American, and it is used in the industrial production of this important medicine. The scheme of synthesis of syntomycine is as follows:



In 1957, M. M. Shemyakin and N. K. Kochetkov and collaborators synthesized dihydrosarcomycine -- the closest analogue of sarcomycine -- a new antibiotic discovered by Japanese workers and possessing anti-tumor action. Somewhat later, Shemyakin and his coworkers published a paper on the synthesis of sarcomycine (racemic) itself. Of other studies, mention should be made of the discovery of gramicydine-c (G. F. Gauze, M. G. Brazhnikova).

In the field of the chemistry of vitamins, important studies have been carried out by N. A. Preobrazhensky, D. A.

Bochvar, M. M. Shemyakin, and others.

Terpenes were the subject of classical researches of Russian chemists (particularly E. E. Vagner). During the Soviet period, broad synthetic studies in the terpene series and other bicyclic compounds were carried out by S. S. Nametkin and his pupils. In these investigations, that were begun before the October Revolution in 1917, a discovery was made of second-order regrouping that which received the name of "Nametkin regrouping". Of other studies in this field, mention should be made of the investigations of A. E. and B. A. Arbuzov (studies of the composition of terpentines of various species of home-grown coniferous trees), N. A. Prilezhaev (oxidation of terpenes by peracids and the study of the properties of α-oxides of terpenes), V. E. Tishchenko (studies of the regrouping of pinene into camfene over a contact agent, which permitted production of camphor from turpentine), and others.

The chemistry of high-molecular compounds has seen great development in the U.S.S.R. and made possible the building of such industries as the production of synthetic rubber, plastics, artificial and synthetic fibre, varnishes and dyes, leather substitutes, electrical insulation, etc. The noted Soviet chemists, S. V. Lebedev and P. P. Shorygin, were the founders of the most important trends in the chemistry of high-molecular compounds (synthetic rubber, artificial fibre). The polymers of styrene and its homologues were studied by P. P. Shorygin and N. V. Shorygina, and also by other workers. We have already mentioned studies connected with the polymerization of vinyl esters and acetylene alcohols. It may be added that on the basis of the latter, I. N. Nazarov obtained a fine adhesive (carbinol glue). Soviet researches have likewise studied many other high-molecular substances that have found important applications.

Of recent work, mention should be made of the investigations of A. N. Nesmeyanov, R. Kh. Freidlina and their coworkers on telomerization of olefines with carbon tetrachloride and chloroform. Studies were made of the chemical transformations of tetra- and trichloro-alkanes obtained by these reactions. The conditions have been worked out for the reaction of telomerization of ethylene and carbon tetrachloride. These conditions have made it possible to set up experimental production of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and their processing into intermediates of industrial organic synthesis for synthetic fibre ("enant", "pelargon"), plasticizers, lubricants, and other valuable products.

In the study of the most common natural polymer -- cellulose -- important work has been done by V. I. Ivanov and his coworkers. It has been demonstrated that the real molecule of cellulose includes bonds that possess a high reactive ability. The chemical nature of anomalous links is determined by the presence of carbonyl and carboxyl groups of the second, third, and sixth carbon atoms of the glucose link. The original breakdown of the macromolecule occurs mainly at these weak points and results in alterations of the physical and chemical properties of cellulose as a polymer, while, practically, it leads to a deterioration of the working properties of the articles. As was earlier established, the chain molecule of cellulose can contain over 10,000 glucose residues in a chain. V. I. Ivanov, B. A. Zakharov and others have theoretically shown and experimentally corroborated the fact that the properties of cellulose depend on homogeneity in the degree of polymerization. The permolecular structure that determines the properties of cellulose is dependent on the degree of molecular homogeneity. Transposition of the degree of polymerization of the dominant fraction into a high-molecular region is accompanied by enhancement of the physico-mechanical and physico-chemical properties. The data obtained open up scientific promise of obtaining durable and superdurable articles of cellulose (cord, fibre, paper, film, varnishes, etc.).

The physico-chemical investigations into the field of high-molecular substances will be considered later on. Here mention should be made of the studies of V. V. Korshak and co-workers in the field of polycondensation, that have led to a theory of this process which is important in the production of synthetic materials: lavsan, anid, and others. Investigations connected with the production of a new polymer material, polypropylene, have been successfully concluded under the supervision of A. V. Topchiev.

Physical chemistry was represented in pre-revolutionary Russia by a galaxy of investigators (N. N. Beketov, I. A. Kablukov, V. A. Kistyakovsky, D. P. Konovalov, and others). Yet it really flourished only during the Soviet period. At present the Soviet Union has several large physico-chemical schools successfully developing theoretical problems in physical chemistry and offering substantial aid to the national economy of the country.

N. N. Semyonov, his pupils and coworkers have made outstanding progress in the development of the theory of chain reactions. In 1926, N. N. Semyonov, Yu. B. Khariton, and Z. F. Valta found that phosphorus vapour ignites and burns only when the pressure of the oxygen exceeds a certain limit, a critical value. Two years later, N. N. Semyonov explained this phenomenon by means of his theory of chain ignition worked out on the basis of the concept of branched chain reactions: the self-acceleration of such a process in isothermal conditions is due to the fact that as a result of the reaction of active molecules there appear new active molecules in large quantities. This is what leads to progressive acceleration of the process, which culminates in ignition if the probability of increase in number of active molecules, or the probability of branching of the chain, exceeds the probability of disappearance of the active molecules as a result of their deactivation and rupture of the chain.

The principal ideas of the chain theory were subsequently developed in studies of the reactions of ignition and explosion in cases of the interaction of hydrogen and oxygen (A. V. Zagulin, A. A. Kovalsky), chlorine and hydrogen (A. Trifonov), and the oxidation of hydrocarbons (A. A. Kovalsky, P. A. Sadovnikov, N. M. Chirkov). The exponential law of isothermal acceleration of branched chain reactions that N. N. Semyonov had deduced theoretically was confirmed by experiment. N. N. Semyonov enriched the chain theory with new concepts -- on the continuation, branching, rupture and interaction of chains, and on degenerated explosions and degenerated branchings. A rigorous quantitative theory of a heat nonisothermal explosion was worked out together with D. A. Frank-Kamenetsky. Similar views were later utilized by physicists in constructing the theory of thermonuclear reactions. Semyonov's coworkers, Yu. B. Khariton and Ya. B. Zeldovich published, in 1939-40, the first, fundamentally correct theory of the chain reaction of uranium fission. It is interesting to note that in the experiments of A. B. Nalbandyan having to do with influencing the process of chain ignition, use was made of metal rods that were inserted into the vessel with the combustible mixture or removed from it. This technique proved to be similar to the control operation in nuclear reactions by means of rods that intercept neutrons.

During the past 25 years, chain reactions have been studied extensively in all countries and have confirmed Semyonov's view that this type of chemical process is very widespread. Of the Soviet studies, we may mention the investigations of N. M. Emanuel on problems of homogeneous catalysis and chemical induction in slow branched chain reactions. In the mechanism of oxidation reactions he detected the presence of macroscopic stations separated in time, which made it possible to control the chemical process by various actions that change in the course of the reaction. For example, he suggested using catalysts or ionizing radiations for the initial stages of chain oxidation reactions developing in a gaseous or liquid medium. The use of these agents in subsequent stages of the process is superfluous. These researches have opened up new pathways in the control of production processes.

S. S. Medvedev and his coworkers have given an experimental substantiation of the chain reaction of polymerization reactions. M. B. Neiman has demonstrated that oxidation of hydrocarbons develops by the mechanism of degenerated branchings. V. V. Voevodsky has worked out the chain mechanism of the thermal decomposition of olefines. The chain theory is finding ever-expanding applications in catalytic reactions. A. A. Kovalsky has shown that many catalytic reactions that begin at the surface of a catalyst, later continue in the gaseous phase following the chain mechanism.

The great value of the scientific achievements of N. N. Semyonov in the field of the mechanism of chemical reactions earned him the 1956 Nobel Prize in chemistry.

The nature of active particles arising in the chain reaction was studied by V. N. Kondratiev and his coworkers. He worked out precision techniques for detecting free atoms and radicals in conditions when the chemical reaction is developing (the spectroscopic method of linear absorption, the method of catalytic recombination). It was thus possible to establish the formation of OH radicals and H atoms in the reaction zone of hydrogen combustion, of the CS-radical in the combustion of carbon bisulfide, and of sulphur monoxide SO in the initial state of the oxidation of hydrogen sulphide. It was shown that the reaction between hydroxyl and the fuel is the basis of processes of combustion.

Of researches carried out in recent years, mention should be made of determinations of the energy content of a number of free radicals and comparisons of their energy with the mean binding energy in the initial molecules. These investigations aimed at determining the reactive capacity via the energy characteristics of free radicals of substances that can participate in chain reactions. V. L. Talrose and E. L. Frankevich made a study, in an ion source of a mass spectrometer, of a reaction between free radicals, originating as a result of electron impact, and nondissociated molecules of other substances. This method permitted determining precisely the affinity of a number of organic molecules to a proton.

Using the method of paramagnetic resonance, A. A. Berlin and coworkers studied the destruction of polymers under mechanical crushing. It was found that up to 10^{18} free radicals are formed per gram of substance. In searching for conditions of the regeneration of these radicals there will open up the possibility of utilizing polymers in heterogeneous catalysis.

L. A. Blumenfeld has investigated enzymatic processes by the method of paramagnetic resonance, and has come to the conclusion that there is a free movement along the peptide chain. Under the conditions of the reaction, this converts the molecule of the enzyme into a free radical. An idea has been expressed of the possibility of producing semiconductor polymers characterized by regular alteration of single and double bonds.

Investigations into reactions with the formation of free radicals are expanding all the time. Ya. K. Syrkin and E. N.

Guryanova have shown that reactions of isotopic exchange of sulphur of a number of organic compounds proceed in accordance with the radical mechanism. Free radicals are also detected in the processes of oxidation and cracking of hydrocarbons (V. V. Voevodsky).

The discovery, by the Soviet physicist E. K. Zavoisky, of electronic paramagnetic resonance in 1944 has exerted a great influence on the development of physico-chemical research. Studies of the shape of paramagnetic resonance curves and their fine structure yield valuable information on the ground state of paramagnetic atoms in the given compound and about the magneto-dipole and exchange interaction between them. Measurement of electronic paramagnetic resonance is used for direct determination of the concentration and structure of free radicals that originate in various chemical systems, for example, under the action of ionizing radiations. This method is one of the most sensitive modern techniques of instrumental physico-chemical analysis and has found wide application in all countries, because its absolute sensitivity runs up to 10^{13} unpaired spins in measured volume.

In the Soviet Union, electrochemistry has made great strides. Such large-scale branches of production have been set up as that of aluminum and magnesium, nonferrous metals, chlorine, alkalis, and oxidizers. The industry of chemical sources of electricity and the use of methods of the electroprecipitation of metals have seen considerable development.

A particularly significant contribution to the development of electrochemical science has been made by the school of A. N. Frumkin, whose works have exerted a big influence on the development of electrochemistry in other countries as well.

Frumkin's research underlies present-day views on the structure of surface layers at interphases and the mechanism of processes occurring in these layers. These studies in large measure contributed to the establishment and development of the new science of electrochemical kinetics, which has become the basis of the theory of chemical sources of current, electrolysis, corrosion of metals and polarographic analysis; they have likewise been of value to certain divisions of colloidal chemistry, the theory of adsorption and heterogeneous catalysis.

A number of new precision methods of electrochemical research have been developed and applied diversely to the study of the structure of surface layers -- double ionic layers and adsorption layers of surface-active substances on various interphase boundary. These include methods of determining potential jumps on an aqueous solution - air boundary, measurements of the capacity of a double layer, and investigations of the kinetics of electrode processes by means of alternating current in a broad frequency interval.

A. N. Frumkin has introduced a new and important electrochemical characteristic of metal -- the potential of a zero charge of its surface. It was demonstrated that this potential, which corresponds to the absence of a double layer of ions on a metal-electrolyte boundary, depends on the nature of the dipole solvent and the metal and that the potential difference of the zeroth charge for various metals is, to a first approximation, equal to the difference of their contact potentials. Thus was clarified one of the most involved problems of electrochemistry on the interrelations of the electromotive forces of galvanic circuits and contact potentials in a vacuum.

Frumkin's studies have led to the establishment of a number of relationships between the kinetics of electrochemical processes and the structure of the surface layer. These concepts were originally applied to an especially important reaction of hydrogen evolution and made it possible, for a number of cases, to give a rigorously quantitative theory of this process. They were subsequently generalized to other electrochemical processes; particularly interesting results have been obtained in recent years in the study of the electrical reduction of anions.

A. N. Frumkin likewise made a study of the phenomena of adsorption of organic substances on various interphase surfaces, which enabled him to establish relationships between the orientation of dipole bonds and the origin of potential jumps, and also to grasp the peculiarities of adsorption processes occurring on metal surface. The latter is especially important for an understanding of the action of corrosion inhibitors. He was the first to give an interpretation of the process of the dissolving of metal (as exemplified by the decomposition of amalgams) as a result of the parallel development of two conjugated electrochemical processes occurring at one and the same potential.

In the course of a number of years, A. N. Frumkin and his coworkers have devoted particular attention to the mechanism of processes occurring in chemical sources of electricity, which has been of importance in the development of this branch of industry.

The ideas developed by Frumkin are in wide use in present-day electrochemistry and have been utilized by Soviet scientists (O. A. Esin, M. A. Loshkarev, L. I. Antropov, S. V. Karpachev, B. V. Ershler, B. N. Kabanov, Ya. M. Kolotyrkin, V. I. Veselovsky, Ya. V. Durdin, etc.).

A big contribution to the electrochemistry of molten salts has been made by the work of Esin, Karpachev and other electrochemists of Sverdlovsk. To illustrate, they were the first to investigate, broadly and accurately, the electrocapillary phenomena in molten electrolytes. These are of considerable theoretical interest and are very important for an understanding of a number of peculiarities of the electrolysis of melts.

The work of B. V. Ershler, B. N. Kabanov and Ya. M. Kolotyrkin place a firm foundation under the adsorption theory of passivity, according to which there is no necessity to create solid protective layers for the passivation of metals, it being in many cases sufficient to alter the kinetics of the processes occurring on the surface of the metal, under the influence of adsorption phenomena.

Recently, Ya. M. Kolotyrkin and his coworkers in the Karpov Physico-Chemical Institute made broad use of the potentiostatic method for investigating the mechanism of passivation of metals. This made it possible to determine the electrochemical behavior of metals in the transition region between the active and the passive state that had remained inaccessible to observation in the earlier methods of investigation.

A definite contribution has been made to the development of the theory of electrocrystallization of metals and elaboration of methods of electric precipitation of metals by A. T. Vagramyan and K. M. Gorbunova.

In the works of Vagramyan and his coworkers it was shown that the rate of electrochemical reactions on separate sections of the electrode is not homogeneous and consists of active and passive portions. In the electric precipitation of metals, the surface state of the electrode is constantly changing, thus complicating the study of electrode processes. A new method was worked out that made it possible to establish, for a series of metals, the dependence of magnitude of overvoltage not on the apparent but on the true current density, with account taken of the actively increasing surface of the electrode. Establishment of a relationship between the magnitude of polarization and the true current density permitted elaborating an electrochemical technique of determining the adhesion of the electrolytic precipitate to the lining. These studies likewise demonstrated that the difficulties that arise in electric precipitation from aqueous solutions of such metals as molybdenum, tungsten, titanium, and others are related to their inclination to rapid passivation.

A. T. Vagramyan developed the concept of the mechanism of electric precipitation of chromium, according to which the electric reduction of chromium takes place not from the ions of the solution but directly from the products that form a film on the surface of the electrode. Complex anions of the type MnO_4^-, ReO_4^-, SeO_4^{2-} and others may help to make up the film, and, consequently, may be reduced on the electrode together with the chromium. Proceeding from these concepts it was possible to work out methods of electrolytic production of new alloys Cr-Mn, Cr-Re, Cr-Se.

K. M. Gorbunova, utilizing in addition to the electrochemical methods also methods of roentgenostructural analysis, made a study of the mechanism of formation and structure of the surface phases of metals, which phases arise in the process of electrocrystallization. Resulting from numerous investigations, partly conducted with single-crystal cathodes, there were formulated certain general regularities that determine the structure of metal precipitates and the phase structure of alloy coatings. These studies were the first to interpret qualitatively the elementary acts of the process of crystal growth -- periodic layer-formation on the faces. The growth of a filament-like crystal served as a model of this process.

K. M. Gorbunova and her collaborators have been devoting of late particular attention to the study of a peculiar type of cryptocrystallic precipitate with grossly disrupted structure, right up to amorphous. It turned out that this type of structure is peculiar to a number of practically important coatings, including precipitates of nickel and cobalt that arise in the process of their chemical reduction by hypophosphite.

These studies have considerably expanded the possibilities of a rational regulation of the properties of electrolytic coatings of metals and alloys, for instance, with respect to their brilliance or hardness, their magnetic or electric characteristics.

Research in the field of electrochemistry gave impetus to the development, by V. G. Levich, of a new and original trend in physical chemistry -- physico-chemical hydrodynamics. Its aim is the study of the effects of the medium on the nature of chemical processes, and, on the other hand, of the effects of physico-chemical factors, particularly, of surface phenomena, on the movement of the liquid. V. G. Levich has worked out a quantitative theory of convective diffusion of matter in a moving fluid, which he applied to the kinetics of heterogeneous chemical and electrochemical processes on interface boundaries. He has developed a theory of a number of elementary processes of chemical technology (the barbotage process, fragmentation of bubbles and diffusion to bubbles and gas jets), extraction, diffusion to flowing film under conditions of the scrubber process, etc. The theory of mass transfer in gas flows, the theory of heat transfer in fluid metals, and the theory of convective diffusion in double liquid mixtures in a critical state have been developed, and a series of other problems in physico-chemical hydrodynamics have been solved.

V. A. Kistyakovsky laid in our country the foundations of research into the processes of corrosion and the fight against it. This division of electrochemistry, which is particularly important for the national economy, has seen extensive development in the works of G. V. Akimov and his pupils (N. D. Tomashov, I. L. Rozenfeld), in which a theory of multielectrode systems has been developed, permitting the determination of how each component part of the complex system is to behave as regards corrosion. A theory has been developed of structural corrosion and the role of local elements, the mechanism of processes in corrosion in the presence of atmospheric oxygen clarified, and the nature and protective properties of oxide films studied. These studies have led to substantial practical results in the establishment of methods to protect subterranean and marine structures from corrosion and in the development and introduction of new corrosion-proof alloys and grades of stainless steels.

Research in the field of colloidal chemistry has developed along different lines. In connection with the growth in applications of polymer materials there has been a considerable expansion of studies of lyophilic colloids (A. V. Dumansky, S. M. Lipatov, V. A. Kargin and others). Valuable conclusions were made for soil science and the food industry during studies of the properties and stability of colloidal substances depending on the particle size in the dispersive phase (N. P. Peskov, A. V. Dumansky, and others). Fundamentally new results have been obtained from studying the effects of adsorption of surface-active substances on the properties of dispersive systems (P. A. Rebinder and coworkers). Also under study was the problem of the origin and destruction of aerosols (B. V. Deryagin, I. V. Petryanov, P. S. Prokhorov, and others).

P. A. Rebinder and his colleagues have demonstrated that the principal properties and stability of dispersive systems are determined by the peculiarities of surface (adsorption) layers on a highly developed phase boundary and, above all, by the structural-mechanical properties of these layers. Regularities were established in the effects of adsorption layers of oriented molecules of surface-active substances on the wetting of solid surfaces, and it was shown that intense hydrophobization (reduction in water-wetting) requires a chemisorption bond of the polar group of the surface-active substance with atoms (ions) of the solid surface. These regularities determine the action of flotation reagents -- collectors.

Elucidation of the mechanism of formation, structure and properties of adsorption layers on various interface surfaces made it possible to substantiate scientifically the choice of synthetic surface-active substances to be used as wetting agents and dust-catching additives, detergents, amulgators, foam-formers, dispersing agents, and suspension stabilizers (A. B. Taubman, A. A. Trapeznikov, et al.).

Studying the development of surfaces in solids in the process of their deformation and destruction, P. A. Rebinder established new and extremely general phenomena of adsorption reduction of durability. Elucidation of the regularities and mechanism of these phenomena, which have come to be known as the "Rebinder effect", on metals and non-metallic solids has led to a broad practical application of adsorbing substances as lubricants for simplifying and improving mechanical working of metals by pressure and cutting, additives for intensifying the fine grinding of solid materials, for improving detergent solutions in drilling, etc.

Recently, Rebinder, V. I. Likhtman, V. N. Rozhansky and others have shown that fusible metals used as the liquid medium or surface-active admixtures can bring about the greatest reduction of the durability of metallic single crystals, converting them from perfectly plastic into brittle. These works indicate not only the ways of simplifying mechanical working of solids, but also the possibility of controlling their structure and properties in the direction of greater durability, particularly at elevated temperatures, which is attained by eliminating surface-active media and admixtures or appropriate training in surface-active media.

P. A. Rebinder, E. E. Segalova, N. N. Serb-Serbina, L. V. Ivanova, and others have clarified the mechanism and regularities of formation of spatial structures in suspensions and colloidal solutions, and also in solutions of high-molecular compounds, especially in connection with the action of active fillers. The development of concepts concerning two basic types of structures - coagulation-tixotropic, which reversibly re-establish themselves after destruction, and condensation-crystallization structures, which are extremely durable and irreversibly disintegrate, was widely used in soil studies to determine the structural-mechanical properties of soils and clay types of varying humidity. These studies likewise led to the development of a theory of solidification of mineral binding agents, a theory of cement concretes and asphalt-concretes with optimal properties - extra durability and resistance (N. V. Mikhailov, and others). Studies were made of processes of spontaneous dispersion that lead to the formation of stable (reversible) colloidal systems.

The development of these new divisions of colloidal chemistry and the physico-chemistry of surface phenomena on the borderline of solid-state molecular physics, the mechanics and technology of materials, has led to the development of a specific borderline branch of science - physico-chemical mechanics. Its aim is to control the mechanical properties of solids of different types and the processes of their deformation and breakdown by the joint action of alterations in temperature, stressed state, and also through physico-chemical effects of the medium and of impurities. At the same time, physico-chemical mechanics solves the problem of obtaining solids and structuralized systems, and also building and constructional materials with predetermined mechanical properties and structure, and the problem of optimal working techniques (pressure, cutting, grinding). Physico-chemical mechanics is becoming the natural scientific basis for the production of building and constructional materials with predetermined properties and structure, and the substantiation of optimal regimes of mechanical working.

B. V. Deryagin has worked out an electrical theory of coagulation and stability of hydrophobic dispersion systems - suspensions, emulsions, and colloidal solutions, which theory is based on consideration of the wedging pressure of diffusional double layers of ions on particle surfaces and of van der Waals forces of adhesion between them. B.V. Deryagin and his colleagues were the first to measure directly the van der Waals forces of attraction between solids, and thus to substantiate the present theory of the action of these forces over comparatively long distances. He also developed an electrical theory of adhesional detachment of films and coatings from solid surfaces, substantiated the phenomena of charge separation, that is, the formation of double electrical layers in such sufficiently rapid detachment.

Studying the kinetics of the formation of colloidal particles in solutions by means of electron-microscope and, simultaneously, by electronographic observations, V. A. Kargin and co-workers demonstrated that the new solid phase arises at first in the form of amorphous balls of comparatively large size, which then crystallize and disintegrate in the given medium into tiny crystalline particles that form the micelles of the colloidal solution. These studies are closely related to a large group of investigations of Kargin in the field of the sols of aluminum hydroxide and alumino-silicon colloids, which are of special significance for problems of soils and ground studies.

V. A. Kargin, N. V. Mikhailov, V. L. Karpov, and others have shown that the state of polymers, which had earlier been considered crystalline, prove in a number of cases to be amorphous (cellulose and its derivatives). As a result of studies of the dependence of deformational forces on the temperature, with account taken of relaxation phenomena (thermomechanical curves), important regularities were established of mutual transitions of high-elastic vitreous and viscous-flowing states of polymers in their connection with chain structure and flexibility of linear macromolecules. These investigations led to the development of important industrial methods of producing extra-durable fibres and films on the basis of high-molecular compounds as a result of orientation during tension.

Conducting investigations in the thermodynamics of formation and properties of polymer solutions, V. A. Kargin, S. P. Papkov, A. A. Tager and others established that such solutions, in typical (good) solvents, are true solutions and do not possess micelle structure. Increasing the concentration of the polymer leads to spatial structure-formation, that finds expression in jellying as a result of interaction between macromolecules.

The works of N. A. Fuks, I. V. Petryanov and B. V. Deryagin and their coworkers have led to the solution of a series of problems of aerosols, which are important in geophysics and meterology, and also for industry and agriculture (charging of aerosols, the mechanism of their stability and breakdown, control of these processes, particularly in fogs and clouds).

Research into the chemistry of surface phenomena was begun in the U.S.S.R. by the classical studies of N. A. Shilov on adsorption of electrolytes on various adsorbents and, in particular, on active carbons. N. A. Shilov developed concepts on the origin (on carbon surfaces as a result of chemical adsorption of oxygen) of surface chemical compounds capable of exchange with the ions of electrolytes. Actually, these studies contained in embryo the idea of ion-exchangers that have now attained such great importance. N. A. Shilov made a large contribution to the study of the process of absorption of gases and vapours from an air current by layers of adsorbents and in laying the foundation of the theory of adsorption dynamics. These investigations were developed by his pupils, M. M. Dubinin, K. V. Chmutov, and others.

M. M. Dubinin and his coworkers (A. V. Kiselev, L. V. Radushkevich, V. M. Lukyanovich, and others) have developed precision techniques of study of adsorption phenomena and measurements of the heats of adsorption of gases and vapours. They have carried out fundamental investigations into physical adsorption both of individual substances and their mixtures. A theory was developed of adsorption on adsorbents with an energetically inhomogeneous surface, which theory establishes relations between the magnitudes of adsorption of gases and vapours, their physical properties and the porous structure of adsorbents, and quantitatively describes the process of adsorption in a broad interval of temperatures and pressures that include the critical region. Methods of activating carbons were developed and extensive investigations into the pore structure of active carbons were carried out by composite methods, including electron microscopy. Refinements were introduced into the potential theory of adsorption of vapours of organic substances in the pores of carbon, which theory has led to simple equations of adsorption isotherms, the form of which depends on the nature of the porosity. Studies have been made of adsorption from mixtures of vapours, and also of the dynamics of adsorption by a layer of adsorbent from a flow of a mixture of gases. A theoretical study has been made of capillary condensation around points of contact of spherical shaped particles.

A. V. Kiselev and his coworkers have made theoretical and experimental studies of the energy of adsorption forces and the effect on adsorption of vapours and solutions of modifications in the geometrical structure of the adsorbents and chemical modification of their surfaces. The energy values of adsorption both of simple and complex molecules, calculated only on the basis of the electric and magnetic properties of the adsorbent and adsorbate and their geometrical structure have proved to correspond closely with values of the heats of adsorption measured in sensitive calorimeters. Established is the radical effect of the degree of hydration of the surface on the adsorption energy of molecules capable of forming a hydrogen bond, and also of molecules with a sharply non-uniform distribution of electron density (unsaturated and aromatic hydrocarbons). Isotherm equations have been obtained for mono- and polymolecular adsorption. These equations take account both of adsorbate-adsorbent interaction and adsorbate-adsorbate interaction.

By chemical modification of surfaces in various reactions, A. V. Kiselev, and A. Ya. Korolev succeeded in changing, by tens and hundreds of times, the adsorption properties of unit surface of solids - adsorbents and fillers for high polymers. The method of infrared spectroscopy was used to investigate alteration of the chemical surface structure and of adsorption properties. A theory has been worked out on the corpuscular structure of the skeleton of porous adsorbents - xerogels. A theoretical and experimental study has been made of the effect of this structure on adsorption and capillary condensation of vapours.

V. K. Semenchenko and coworkers have carried out extensive theoretical and experimental research into surface phenomena in metallic and salt melts. B. V. Ilin has investigated the heats of wetting of solids by various liquids.

K. V. Chmutov and his coworkers have studied in detail the static and kinetic characteristics of numerous samples of Russian ion-exchange resins, and have carried out extensive investigations in the field of complex-forming chromatography by means of tracer techniques, and have accomplished hydraulic modelling of sorption columns.

Catalysis phenomena have been comprehensively and broadly studied in the U.S.S.R. In 1918, L. V. Pisarzhevsky advanced the idea of the participation of electrons of the catalyst in catalytic processes and of the relationship of the electronic properties of the solid with its catalytic properties. Developing these concepts, S. Z. Roginsky established new regularities that relate the catalytic properties of solids to the position of the component elements in the periodic table, and demonstrated the relationship between the catalytic properties of substances and their semiconducting properties.

F. F. Volkenshtein has developed a theory of chemisorption on semiconductors in accordance with which the free electrons and holes are the centres of adsorption. In other words, this role is played by free valences of the adsorbent wandering about on its surface. Each act of chemisorption is accompanied by a rupture of the valence bond inside the molecule being sorbed, its transformation into a radical or its dissociation into two radicals. The author demonstrated that as the surface fills up, more and more new adsorption centres should appear, and they should come to the surface faster than the filling proceeds. The adsorption and catalytic properties of semiconductors are closely interrelated. F. F. Volkenshtein has theoretically substantiated the supposition of a connection between the electric conductance of a semiconductor and its catalytic activity, and this has been corroborated in the studies of Soviet and other authors.

S. Z. Roginsky and his coworkers have made broad studies of the physical chemistry of catalysis; the structure of catalysts, the nature of their active surface, and regulation of the properties of catalysts by the introduction of various additives. The phenomenon of gaseous promoting of metallic catalysts was discovered, and the chemical conception of an active surface was developed. According to this conception, microimpurities and deviations of composition of the solid from stoichiometry play an important role in creating active structures. On this basis, S. Z. Roginsky, O. M. Todes, and L. Ya. Margolis proposed a method of chemical modification of catalysts. Together with N. P. Keier they worked out (using tracer techniques) a differential isotope method of studying catalysts that made it possible to obtain new and valuable information on the nature of an active surface.

A big contribution to the study of phenomena of heterogeneous catalysis has been made by the researches of A. A. Balandin, who has proposed the multiplet theory, in accordance with which the most important thing in catalysis is attributed to structural and energy factors. A. A. Balandin demonstrated that the elementary catalytic act is possible only in the case of specific relationships of the interatomic distances in the reacting molecules and in the crystal lattice of a catalyst (the principle of structural correspondence), and also pointed to ways of taking into account the roles of such factors as the energy of bonds that form and disrupt in the course of reactions (including bonds in the intermediary complex with catalyst), adsorption potentials and heats of reaction (the principle of energy correspondence). These two principles make it possible to account both for the specificity of the catalytic reaction and the specificity of catalysts necessary for it, and it likewise opens up the possibility of predicting the behaviour of molecules on the surface of a catalyst.

A. A. Balandin developed a method of studying adsorption on catalytically active centres including the measurement of its free energy, heat and entropy, which is extremely important for heterogeneous catalysis, since the latter is always preceded by a stage of adsorption. On the basis of reactions of dehydrogenation of hydrocarbons, and also dehydrogenation and dehydration of alcohols, it was shown that the binding energy between a molecule and the catalyst may be determined from the kinetics of the process. These studies confirmed the necessity of orientation of the atoms of the reacting molecules with respect to the catalyst.

Utilizing the so-called sextet model proposed by N. D. Zelinsky (Fig. 2), the multiplet theory accounts for the catalytic dehydrogenation of six-member cycles on metals, if the molecule entering into the reaction is arranged flat on the surface of platinum, palladium, nickel and other metals. The theory explains why only metals of a definite crystalline structure and with specific atomic radii prove to be active in this case, why only six-member rings can be dehydrogenated in accordance with this mechanism, and why they form only aromatic, and not saturated systems.

Fig. 2. Scheme of catalytic dehydrogenation of a six-member cyle.

The multiplet theory predicted the activity of rhenium and several alloys as the catalysts of reactions of dehydrogenation. It also explained the dehydrogenation (discovered by Balandin) of cyclohexanole on the oxides of chromium, molybdenum and other metals. In this case the molecules are oriented along the sides of the crystals. According to the multiplet theory, the orientation of molecules along the sides can condition dehydrogenation of other systems too, for example, of cyclopentane and of aliphatic hydrocarbons such as butane (see Fig. 3), thus, the restrictions observed in the case of metallic catalysts are removed if we use oxide catalysts.

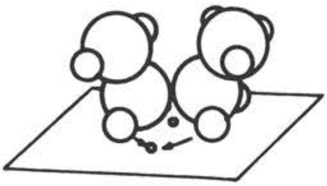


Fig. 3. Scheme of catalytic dehydrogenation of butane.

A big step forward is the creation, by Balandin on the basis of model concepts of the multiplet theory, of a harmonious classification of doublet and triplet heterogeneous-catalytic reactions. This classification conveys the structure of the intermediate (multiplet) complex that forms on the catalyst, and not only embraces all already known doublet and triplet reactions, but also those that are possible in principle. The mathematical, physical, and chemical aspects of the multiplet theory have enabled Balandin and his school to attack directly the solution of the complex problem of rational selection of catalysts.

Of great importance for the development of the theory and practice of catalysis are the works of the Soviet scientists V. A. Roiter, G. K. Boreskov, and D. A. Frank-Kamenetsky devoted to the effect of transfer of matter and heat on the rate of macrokinetic heterogeneous catalytic reactions.

Research into chemical thermodynamics has been rather extensive in the U.S.S.R.

Measurements of thermodynamic functions of individual inorganic compounds, groups of compounds, solutions and alloys in connection with theoretical generalizations and practical problems (mostly metallurgical) have been carried out by many researchers who have obtained new data utilized in appropriate tables. Studies have been made of the thermodynamics of sulphides (E. V. Britske, A. F. Kapustinsky), oxides (A. I. Volsky), chlorides (S. A. Shchukarev), tungstates and oxides of tungsten (Ya. I. Gerasimov) and of a number of other areas. There has been much research into the thermodynamics of metals and alloys. An. N. Nesmeyanov and his coworkers have measured the pressure of saturated vapour of many metals and alloys in the solid state using radioactive tracers.

New thermochemical information has been obtained by M. M. Popov, S. M. Skuratov and their colleagues, who have determined the heats of formation of a number of organic substances and the heats of polymerization and polycondensation in the solid phase.

Studies of chemical equilibria in complex mixtures, in particular at high temperatures, has been of great interest to many branches of technology (thermal and catalytic cracking of petroleum products, processes of combustion, etc.). Experimental investigations in this field have been conducted by A. V. Frost, I. N. Godnev, P. G. Maslov, V. M. Tatevsky, and others.

Extremely interesting results have been obtained by I. R. Krichevsky and his coworkers in measuring the solubility of gases in liquids at high pressures (up to tens of thousands of atmospheres). A fundamentally new phenomenon was discovered - the restricted mutual solubility of gases under high pressures and at temperatures above critical.

The theoretical prediction of the possibility of stratification of gas mixtures was made 50 years ago by Van der Waals, but it remained a purely speculative idea and was not taken into account in practical work in laboratories and factories using compressed gases. Its experimental confirmation will exert a big influence on the solution of a number of technological problems concerned with high pressures.

Investigations in the field of photochemical processes have been carried out by A. N. Terenin and his coworkers. They were the first to demonstrate the possibility of direct photodissociation of molecules, in particular the dissociation of ionic molecules of the NaI type into neutral atoms, and also the possibility of the photodissociation of molecules into oppositely charged ions. A. N. Terenin worked out a fluorescent method of studying the photochemical dissociation of molecules, which consists in observing the fluorescence of the products of dissociation upon the irradiation of a given gas (or vapour) by light of different wavelengths. It is thus possible to establish the nature of the primary photochemical act, which is extremely important in studies of the kinetics of photochemical reactions. The fluorescent method has proved especially effective in application to photochemical reactions of aromatic compounds, in particular of dyes. In this case the primary act of irradiation under the action of ultraviolet or visible light is an excitation of a molecule which has absorbed light, without dissociation of the molecule. Terenin worked out a scheme of the energy transformations of the excited molecules and showed the special role of metastable triplet states in the photochemical reactions of aromatic substances. According to Terenin, these active states of the forming biradical play a decisive role in the fading of dyes in the light.

During the past decade, the new branch of physical chemistry, called radiation chemistry, has seen intense development in the Soviet Union. Research is conducted by means of gamma radiation from powerful cobalt-60 sources, with the use of x-irradiation from special equipment; the action of a beam of high-energy electrons, or directly in the channels of uranium reactors.

New data have been obtained in the solution of various radiation-chemical problems. Studies of the radiolysis of water and aqueous solutions in the works of P. I. Dolin, B. V. Ershler, and M. A. Proskurnin have expanded our knowledge of the mechanism and kinetics of the processes. It was established, for instance, that the introduction, into a solution under irradiation, of acceptors that selectively react with one of the radical products of radiolysis of water makes it possible to make practically total use of the other radical products.

An original trend is the research of radiation-galvanic phenomena that occur on electrodes during the radiolysis of solutions of electrolytes (V. I. Veselovsky and coworkers).

Studies of radiolysis of hydrocarbons in the liquid and solid states have been carried out by A. V. Topchiev, L. S. Polak and others. It has been demonstrated that under the action of radiation, the cracking of n-heptane takes place at lower temperatures than ordinary thermal cracking.

In studies on the radiation oxidation of organic compounds by molecular oxygen, N. A. Bakh and coworkers and B. M. Mikhailov have established that, depending on the nature of the compounds under irradiation and the temperature, radiation chemical processes are either of a non-chain nature or proceed according to the chain mechanism with short chains.

Investigations into radiation polymerization have made it possible to differentiate between ion and radical mechanisms of polymerization that takes place under the action of ionizing radiation (A. D. Abkin), and have shown the great possibilities of the emulsion method of polymerization (S. S. Medvedev).

Wide use is being made of the transformations of polymers under the action of radiation. Valuable results have been obtained by measurement of changes in the mechanical properties of polymers in the very process of their irradiation (Yu. S. Lazurkin, V. L. Karpov and coworkers).

The works of A. A. Balandin and V. I. Spitsyn and their colleagues on the separation of active solids in the radiolysis of aqueous solutions point to a new trend in the use of ionizing radiations. As a result of the action of radiation on solutions of the complex salts of platinum, metallic platinum was obtained which possesses far greater activity in the catalytic reaction of low-temperature hydration of cyclohexane than ordinarily prepared platinum catalysts.

In studies by V. V. Voevodsky and coworkers, nonstable free radicals that arise under the action of an electron beam were measured by the method of electronic paramagnetic resonance directly during irradiation. This methodology made it possible to investigate the kinetics of accumulation of free radicals and their behavior, and also to determine the true concentrations of free radicals in a number of irradiated compounds.

Investigation of elementary reactions that occur in the gas phase under the action of slow electrons (N. N. Tunitsky, V. L. Talrose) has shown the importance of ion-molecular reactions in certain radiation-chemical processes.

P. Ya. Glazunov and A. K. Pikaev have worked out the methodology of obtaining and measuring powerful pulses of electronic radiation and have carried out investigations of the effects of extremely high dosages on radiolithic transformations in aqueous solutions.

V. I. Spitsyn and his coworkers have noted that the radioactive radiation of solids exerts an essential effect on their physico-chemical properties (rate of reactions of isotopic exchange, adsorption properties, etc.). Balandin and Spitsyn and their coworkers have shown that the introduction of considerable quantities of a radioactive isotope into a catalyst can essentially raise its catalytic activity.

In the Soviet Union, wide use is made of tracer techniques with the use of radioactive and stable isotopes in studies of the chemical structure of substances, the mechanisms of reactions, the stability and nature of atomic bonds in molecules and for determining many physico-chemical constants. Investigations into reactions of isotopic exchange have permitted obtaining valuable results in various fields of chemistry.

It has already been mentioned that A. A. Grinberg and his coworkers were the first to use radioactive isotopes in studying the structure of complex platinum compounds. It was found that in $[PtX_4]^{2-}$ $-X^-$ systems, the X^- anions arrange themselves (as regards rate of exchange) in the very same series: $CN^- > I^- > Br^- > Cl^-$ as in their capacity to form complexes.

A broad investigation into exchange capacity of inorganic halides with free halogens and their ions was carried out by A. E. Polesitsky, Ya. A. Fialkov, and Yu. A. Nazarenko. They found that the coordination ions of halogens are readily mobile, but exchange is very difficult when the halogen is the central atom of the complex. For example, exchange occurs between IO_3^- and I^-, BrO_3^- and Br^-.

Of very great interest are the studies of A. I. Brodsky, E. I. Dontsova, and others on oxygen exchange in anions of inorganic acids. A study was made of the isotopic exchange of oxygen between O^{18}-enriched water and inorganic compounds at various temperatures. The compounds under study composed a series as to rate of exchange:

$$H_3PO_2 > H_3PO_3 > H_3PO_4;$$
$$H_2SO_3 > H_2SO_4 > HSO_4^- > SO_4^=;$$
$$H_2CO_3 > HCO_3^- > CO_3^=.$$

V. I. Spitsyn and his coworkers have applied the methods of isotope exchange by means of O^{18}, deuterium and radioactive isotopes to the study of the structure of aquopoly- and heteropoly compounds and the mechanism of reactions of their formation in solutions. A study has been made of the rate of isotopic exchange in sulphates of alkali elements at high temperature for the systems $Me_2SO_4 - O_2^{18}$ (V. G. Finikov) and $Me_2\overset{*}{S}O_4-SO_3$ (I. E. Mikhailenko). The rate of exchange of sulphur proved considerably higher than that of oxygen.

A. I. Brodsky and his school have done very considerable research on deuterium exchange in various organic and inorganic substances. These studies have resulted in a subdivision of deuterium-exchange reactions into "fast" and "slow". The fast reactions take place practically instantaneously at any temperature and do not require catalysts. The slow processes of exchange depend in large measure on catalysts of protolitic reactions, and also on the structure of the exchanging molecules and properties of the medium. The reaction of deuterium exchange develops rapidly in the presence of free electron pairs in the atom with which hydrogen is connected. Otherwise the process is slowed down.

A. I. Shatenshtein and his coworkers have studied the effect of the medium on reactions of hydrogen exchange in solutions and have found that its rate in C-H, H-N, H-H, O-H, P-H and S-H bonds depends on the acid-base properties of the solution and the reagents.

G. P. Miklukhin has investigated, by means of deuterium, the pathways of hydrogen in various organic reactions. Ya. M. Varshavsky and S. E. Vaisberg have established the boundaries of applicability of a first-order equation for reactions of isotopic exchange. G. P. Miklukhin and E. N. Guryanova have studied the action of accelerators in processes of vulcanization of rubber and have found that the most active of them easily enter into exchange reactions with elementary sulphur, thus making for a rational selection of such accelerators.

S. Z. Roginsky has worked out the kinetic principles of reactions of isotopic exchange and has systematized vast material on isotopic methods of studying chemical reactions.

Characteristic of the development of Soviet analytical chemistry is the broad introduction into practical work of new physical and physico-chemical methods of analysis. The classical techniques - gravimetric and volumetric - continue to be refined; however, in their practical application they are combined with preliminary chromatography or extraction separation. In precipitation, wide use is made of new organic and inorganic reagents.

Important results have been obtained by the application of methods of physico-chemical analysis to the study of the mechanism of analytical reactions (I. V. Tananaev, A. K. Babko, and their coworkers). In this way it was possible to establish the composition of precipitate, the structure of ions in solution, and to study equilibrium and durability of complex compounds in solutions. K. B. Yatsimirsky has developed a new kinetic method of quantitative analysis with the use of catalysis reactions. This method permits determining ultrasmall quantities of a number of elements in highly diluted solutions. Of great value to analytical chemistry are the radiochemical investigations of V. G. Khlopin and his school in the field of the laws of distribution of microquantities of elements between precipitate and solution, which is of great value for the analytical isolation of elements from ultrasmall concentrations.

Of physical methods of analysis, colorimetry and spectrophotometry are in wide use. They have seen extensive use in determining "traces" of elements in the presence of large concentrations of accompanying substances. In this connection, A. K. Babko and his coworkers have studied, by the spectrophotometric method, the composition and constants of instability of a number of dyed complex compounds. Spectrophotometric investigations into multi-component systems have been carried out by N. P. Komarov and his coworkers.

The polarographic method of analysis has been considerably improved on the basis of studies by Soviet electrochemists. Solid electrodes have been proposed for analysis of molten salts, and a method of amalganic polarography has been worked out. A new trend is the method of oscillographic polarography (Ya. P. Gokhstein and others).

In addition to potentiometry and conductometry, a new method of analysis - coulombometry - has begun to be used. This was first done by M. S. Zakharievsky for determining heavy metals in food products. Later, it found application in other fields.

Valuable results have been obtained by I. P. Alimarin and other authors in the application of radioactive isotopes and their radiations in analytical chemistry. This is accomplished in various ways:

1) the reagent or ion under consideration is labelled with a radioactive isotope;

2) a measurement is made of beta-ray absorption by the substance;

3) radiation reflection is measured;

4) the element under consideration is activated by means of neutrons or other particles (radioactivation analysis).

Radiochemical methods are of the very latest; they permit attaining a high degree of accuracy in determining small quantities of substances (up to 10^{-16} gram and less). The radioactivation method of quantitative analysis has been applied to determine impurities in semiconductors, in particular in metallic germanium. Analytical laboratories are more and more applying methods of isotope dilution, radiometric titration, and others.

An important trend in Soviet analytical chemistry was the broad use of organic reagents in inorganic analysis (V. I. Kuznetsov, L. M. Kulberg, A. S. Komarovsky, and others). A theory of the action of organic reagents was created on the basis of extensive experimental material, the scientific principles of making new organic reagents were worked out, and the use of already known organic reagents (dioxines and others) has been refined. Soviet chemists have synthesized a number of original preparations - "zirconon", "Stillaso", "berillon IREA", "gallion IREA", and others. Also obtained are a number of sensitive organic reagents containing radicals of inorganic acids - "arsenazo", "toron" (V. I. Kuznetsov), and derivatives of sulphorous, tellurous and selenious acids (I. P. Alimarin), as well.

Soviet scientists have proposed a number of new indicators for volumetric analysis. Of particular importance among them is phenylantranylic acid. New indicators are also used in mercurimetric and complexonometric titration. Interesting investigations have been carried out in recent years in the development of the method of "spontaneous reagents".

Considerable progress has been made in various special methods of analysis, such as gaseous, spectral, and others, and likewise in the field of the analysis of organic substances.

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As may be seen from this brief and incomplete survey, Soviet chemical science has made substantial progress. However, characteristic of our science is a constant advancing, a striving to complete as quickly as possible the elaboration of old problems, and the transition to new and more difficult problems. Extensive and diverse problems confront Soviet chemists in the coming years. They will find solution in the spirit of a growing unity of science and practice. Our science must give new methods of intensification of chemical production, it must work out more refined technological processes, and create new and valuable materials with predetermined properties. We consider it necessary that scientists, in cooperation with production people, should arm the national economy with new theoretical investigations, conclusions, recommendations and discoveries that will speed up technical progress in all spheres of economy and in this way contribute to the successful fulfillment and overfulfillment of our seven-year plan.

In the field of chemical science and industry, Soviet scientists pose such problems as the maximum expansion of petroleum chemistry and the development of processes of industrial technology of direct synthesis, which make possible the transition from multi-stage technology to a simpler technology of producing monomers, various synthetic materials and chemical products. We plan to introduce into production new physico-chemical methods of initiating chemical processes, including those utilizing atomic radiations. Electrochemical methods, in particular in organic synthesis, will see appreciable development. An important problem is the further development of the theory of catalysis and the establishment of the scientific principles of selection of catalysts, mainly for working out continuous processes of production of various monomers and other valuable chemical products.

Particular attention is to be devoted to the synthesis of new polymer materials possessing extra resistance to heat, oils, and hydraulic liquids. Exploratory work will be conducted on the synthesis of new high-polymers with an inorganic chain in the molecules, and also purely inorganic polymers.

In the field of inorganic technology there is the problem of developing more economical methods of producing complex and highly concentrated fertilizers, the further refinement of methods of producing various rare elements, and concentrates of radioactive isotopes as sources of radiation.

Fundamental theoretical research paves the way for the technology of future decades. This is why Soviet scientists are planning a huge volume of theoretical and exploratory studies in all the divisions of chemical science.

The synthesis of new compounds is of equal interest to both organic and inorganic workers. However, in inorganic chemistry it will be directed towards the production of derivatives of little studied classes of substances - sulphides, selenides, tellurides, and lower oxides. In organic chemistry, one should expect a further rapid development of syntheses of organo-element compounds and their extension to the entire periodic system. Of particular interest is the extension of sandwich structures into transition elements.

In addition, organic chemistry plans a broad development of research in the field of natural compounds, vitamins and antibiotics.

A list of a small part of the studies planned in physical chemistry would include: profound studies in the physicochemistry of polymers, in particular, of processes of catalytic polymerization, the development of new methods of formation and utilization of free radicals in chemical reagents, the development of methods of obtaining active solids with predetermined properties (sorbents, fillers in colloidal systems, catalysts, etc.), and the expansion of applications of physico-chemical mechanics.

Of course, the general range of scientific research will include analytical chemistry, the methods of which it is planned to make more and more physical and physico-chemical with a wide application of automation in the apparatus used.

There can be no doubt that Soviet chemical science will find original solutions to the problems that confront it. At the same time, the exchange of scientific attainments between scientists of different countries will contribute to a further rapid development of chemical science throughout the world, the practical applications of which create limitless riches for all of mankind.

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NEW DATA ON THE EFFECT OF RADIOACTIVE RADIATION OF SOLIDS AND EXTERNAL RADIATION ON SOME HETEROGENEOUS CHEMICAL PROCESSES

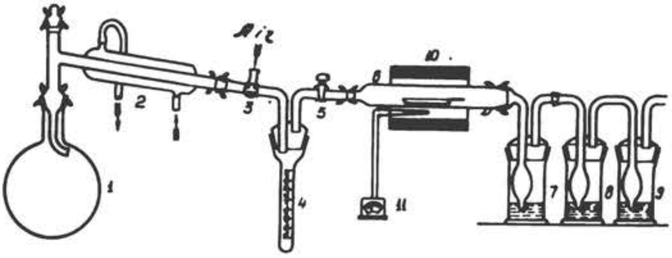
By V. I. Spitsyn

In 1958 the author and his co-workers (I. E. Mikhailenko, V. G. Finikov, V. V. Gromov) reported for the first time information on the effect of radioactive radiation of solids on some heterogeneous processes - isotopic exchange and adsorption out of aqueous solutions (1-3). At the same time the introduction of radioactive sulphur into the catalyst of cyclohexanol dehydration reaction ($MgSO_4$ and Na_2SO_4 mixture) were found to considerably increase its catalytic activity (A. A. Balandin, V. I. Spitsyn et al. (4)).

Continuing the above investigations completely supported the initial observations. Radiochemical activation of the surfaces of solids takes place at radiation doses far smaller than those required for originating radiation-chemical processes as such (decomposition, oxidation-reduction, etc.). The emission of α or β particles by solids must lead to permanent formation, in their bulk and at their surface, of numerous crystal lattice defects, as well as ionized and excited atoms playing the part of charged active centres. As the radioactive preparations (sulphates of alkaline elements, magnesium and barium sulphates, calcium phosphates, cerium oxalate) used by us, are in solid state practically insulators, local electrical fields and electro-neutrality disturbances occurring during the radioactive radiation may live long enough to markedly affect physico-chemical processes that are due to the surface state conditions of a solid.

The effect of the radioactive radiation of S^{35} on the isotopic exchange rate in two heterogeneous systems had been investigated in detail.

The sulphur isotopic exchange in the $K_2\overset{x}{S}O_4-SO_3$ system has been studied at temperature 840° over the range of potassium sulphate specific radioactivities 0.02 - 131 mc/g (2,5). The design of the apparatus used is shown in Fig. 1.



1. The scheme of the apparatus for studying isotopic exchange of sulphur in $K_2\overset{x}{S}O_4-SO_3$ system.

The round-bottomed bulb (1), the cooler (2), the test-tube (4) with a grind and gas-branch pipes, absorption flasks (7), (8), (9) were all made of molybdenum glass, the tube (6) and the boat in it were made of quartz glass. Sixty percent chemically pure oleum was poured into the bulb. The distillation of SO_3 was carried out at temperature 60-70°. Through the cooler and three-way stopcock (3), the two-way stopcock (5) being shut, sulphuric anhydride entered the graduated flask (4), calibrated to point value of 0.05 ml. During the experiment the measured quantity of SO_3 was evaporated by heating and was mixed up with thoroughly dried air supplied by the stopcock (3). Through the stopcock (5) the gas mixture was directed into the reaction zone of the quartz tube (6). A definite sample of radioactive preparation of potassium sulphate was placed into the quartz boat. On passing over the substance sulphur trioxide was trapped in flasks containing concentrated H_2SO_4 (7) and 0.1 N solution of NaOH (8) and (9). Dry air was blown through all the apparatus before and after each experiment. The temperature of the furnace (10) was determined by the pyrometer (11) with platinum - platinum-rhodium thermocouple. During the runs constant temperature was maintained with the accuracy of $\pm 5^{\circ}$. In each run the weight of the sulphate sample was 0.3-0.4 gr., the quantity of SO_3 - 0.3 ml or 0.58 gr. The rate of passage of dry air, carrying sulphur trioxide away, reached 37 l/h. The time of passing SO_3 over the substance studied was 10 minutes. The sulphate sample was in the heated zone of the furnace for 20 minutes. The chosen conditions of experiment (temperature

840°, partial pressure of SO_3 in the passed gas mixture equal to 19.9 mm), as had been found earlier, secure the absence of any ponderable amount of pyrosulphate formed. At the same time potassium sulphate did not reach its melting point yet and did not undergo any thermal dissociation.

Another design of apparatus was tested in which the potassium sulphate sample was placed into a small tube with perforated bottom joined on a grind to the inlet part of the operating tube. In this case the vapour stream of sulphur trioxide passed through the powder. The linear rate of the gas mixture being, for the reasons stated, rather high, considerable powdering of the substance was observed here. Hence the investigation was carried out, according to the above technique, by passing SO_3 over the surface of the K_2SO_4 sample, the constancy of experimental conditions being strictly observed.

Sulphur labelled K_2SO_4 preparations of small activity were prepared by introducing a small amount of active sodium sulphate into their solutions because this compound is a usual source of supplying S^{35}. Its radio-chemical purity was checked by measuring the maximum energy of radiation by means of absorption in aluminum and by estimating its half-life. No impurities of other radio-isotopes were detected. The carrier of S^{35}, stable sodium sulphate, was chemically pure, according to the specification of the supplying enterprise. Highly active samples of $K_2\overset{x}{S}O_4$ were produced by neutralizing labelled $H_2\overset{x}{S}O_4$ with chemically pure KOH.

The prepared solutions of $K_2\overset{x}{S}O_4$ were evaporated to dryness and the residue was calcinated at 800°. Identical specific surfaces of the K_2SO_4 samples were achieved by sieving thoroughly crushed preparations into fractions by special screens. The particle size varied from 0.17 to 0.10 mm.

On carrying out the experiment the active sulphate sample was dissolved in the graduated flask. A definite volume of the solution was evaporated on a sheet of filter paper which was in a round aluminum dish. The sample activity was always estimated under identical geometrical conditions with regard to the end-window counter. The solutions of highly active preparations, obtained after the runs, were diluted in such a way that in all cases the magnitude of impulse counting was approximately of the same order (1500-2000 imp/min.). Four to six experiments on isotopic exchange were made with each preparation of different specific activity. The results were rather well reproducible.

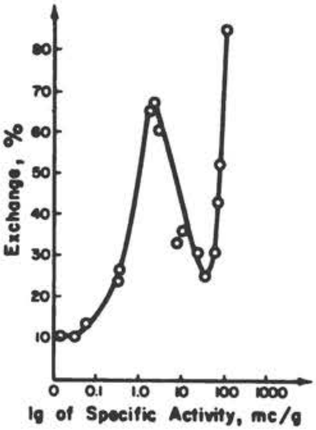
The degree of exchange was calculated by the formula

$$W = (A_0 - A_1)\frac{1}{B},$$

where W - is the percentage of the degree of exchange, A_0 - the activity of initial salt taken as 100%, A_1 - the percentage of the reaction product activity to the percentage of the activity of initial compound;

$$B = \frac{N_1}{N_1 + N_2};$$

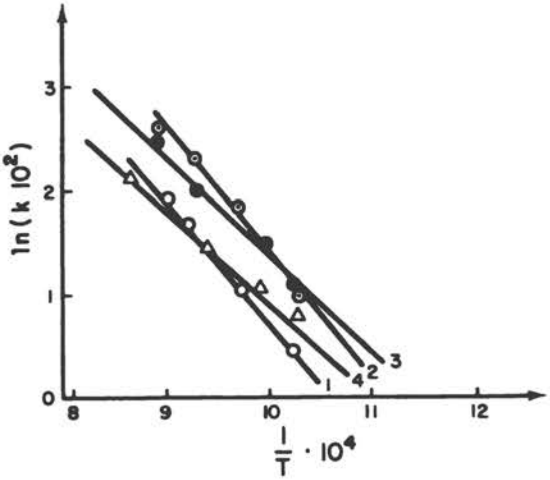
N_1 is the atomic concentration of the element (sulphur) under study in SO_3 passed, N_2 is the atomic concentration of sulphur in the radioactive preparation.



2. The dependence of the exchange ratio of sulphur in $K_2\overset{x}{S}O_4-SO_3$ system on the specific activity of $K_2\overset{x}{S}O_4$.

The results obtained are shown in Fig. 2. When the specific radioactivity of $K_2\overset{x}{S}O_4$ is of the order of 0.02-0.03 mc/g the rate of isotopic exchange is practically constant (11-12% within 10 min.). It begins to increase when the preparation activity surpasses 0.05 mc/g and reaches the maximum at the specific activity of $K_2\overset{x}{S}O_4$ of the order of 2-2.5 mc/g. (the degree of exchange is about 66%). The further rise of S^{35} contents in potassium sulphate leads to the reduction of the rate of exchange. At the specific activity of $K_2\overset{x}{S}O_4$ equal to 35 mc/g the rate of exchange lowers up to 25% within 10 minutes. Then the radioactivity increase of $K_2\overset{x}{S}O_4$ preparations gives rise to a new increase of the degree of exchange reaching 85% at the specific activity of 131 mc/g.

Thus the isotopic exchange of sulphur in the system described is distinctly divided into three phases. Studying the $Na_2\overset{x}{S}O_4$-SO_3 system gave similar results. In this case constants of exchange rate were measured over the temperature range of 700-840°, which allowed to calculate the activation energy of the process. For preparations having the specific activity of 0.02-1 mc/g it turned out to be equal to 23-24 Kcal/mole and for preparations of the activity of 10-25 mc/g it was 18-19 Kcal/mole (Fig. 3).

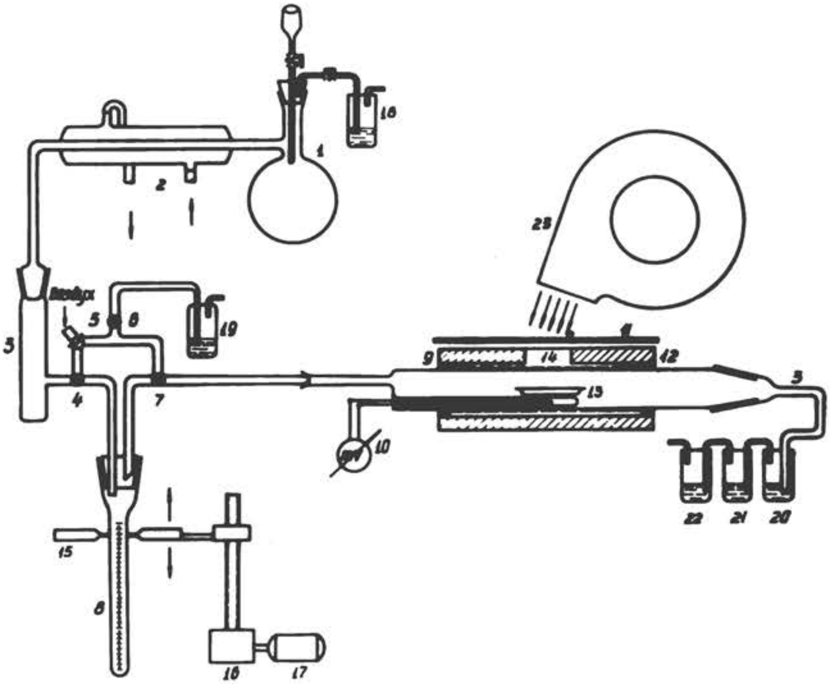


3. The dependence of the rate constant of isotopic exchange reaction in $Na_2\overset{x}{S}O_4$-SO_3 system on inverse temperature. (1) 0.02 mc/g, (2) 1 mc/g, (3) 10 mc/g, (4) 25 mc/g.

The isotopic exchange in the systems investigated appears to take place by the interaction of SO_3 with SO_4^{2-} ions at the sulphate surface and by the formation of $S_2O_7^{2-}$ ions as an unstable intermediate compound. The conditions for their formation will be more favourable with greater quantities of positive charges at the solid phase surface caused by the continuous emission of β-particles. One may consider that this is the reason of the increase of the rate of isotopic exchange over the range of potassium sulphate specific activities from 0.05-2 mc/g. The decrease of the degree of isotopic exchange for preparations having specific activity of 3-35 mc/g depends possibly upon rapid neutralization of positive charges of the active centres by electrons abundantly emitted. At any rate the estimation of the activation energy indicates the different character of these two stages of the isotopic exchange process.

The sharp rise in the degree of exchange by increasing the specific activity of $K_2\overset{x}{S}O_4$ over 35 mc/g is likely to have different mechanism as compared to the first branch of the curve in Fig. 2. One has reasons to suppose that in this case the decisive part is played by purely radiation phenomena produced by the stream of emitted β particles, i.e. the ionization of SO_3 molecules in a gaseous phase as well as the intensified activation of SO_4^{2-} ions and individual atoms of the crystalline lattice of sulphate.

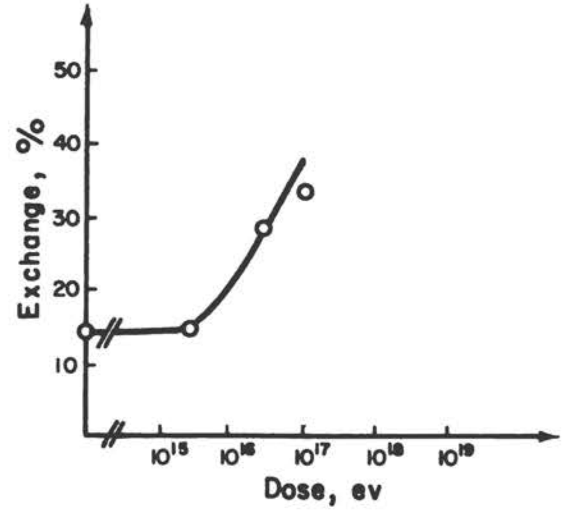
To prove this supposition the isotopic exchange in the $K_2\overset{x}{S}O_4$-SO_3 system was studied at low specific radioactivity of potassium sulphate but under the conditions of external irradiation of the labelled preparation and SO_3 vapors by the electron beam of high energy from the betatron whose construction allowed the outlet of electrons (6). The scheme of the apparatus used is shown in Fig. 4.



4. The scheme of the apparatus for studying isotopic exchange at high temperature under the external electron irradiation. (1) flask with oleum, (2) cooler, (3) receiver for SO_3, (4,5,7) three-way stopcocks, (6) two-way stopcock (8) graduated test tube, (9) reaction quartz tube, (10) millivoltmeter with platinum-platinorhodium thermocouple, (11) lead screen, (12) asbestos heat insulation, (13) quartz boat, (14) slot of the furnace, (15) heating element, (16) reducer, (17) motor, (18,19,20,21,22) washers with concentrated H_2SO_4, (23) betatron chamber.

The installation was mounted on a movable stand, beside the betatron in a special room with concrete walls to protect experimentors from irradiation. The apparatus was distantly operated from a special control panel. The technique of ferrosulphate dosimetry was applied to estimate the radiation doses obtained by potassium sulphate and by gaseous phase.

The external electron irradiation of potassium sulphate and contiguous gas phase containing SO_3, the dose being of the order 10^{15} ev/10 min. (K_2SO_4 samples are about 0.4 gr.), was not shown by the investigation to affect the exchange rate. Increasing the irradiation dose up to 10^{16}-10^{17} ev/10 min. leads to the increase of the exchange rate taking place directly proportionate to the dose logarithm (Fig. 5). No significant potassium sulphate decay was observed during the above experiments.



5. The dependence of sulphur exchange extent in $K_2\overset{x}{S}O_4$ solid -SO_3 gas system on the integral dose of external electron irradiation (within 10 min.).

The external irradiation dose at which the rise of the curve in Fig. 5 begins, approximately corresponds to β-radiation doses obtained by $K_2\overset{x}{S}O_4$ preparations having specific activity corresponding to the beginning of the third section of the curve in Fig. 2. Thus, the interdependence of these phenomena apparently should not give rise to doubt.

It should be emphasized that the emission of β particles by radioactive preparations affects the isotopic exchange ratio far more than the external irradiation by electrons even if the energy of the latter is one order higher. For example, the electron irradiation dose, $3.4\text{x}10^{15}$ ev/10 min., for solid potassium sulphate would be corresponded to by the (own) radioactivity of this salt equal to 2.3 mc/g. The degree of exchange of the above radioactive preparation is about 67% per 10 minutes (5), i.e. 5-5.5 times higher than that for preparations having the activity of 0.02 mc/g. The external electron irradiation by the same dose has no effect on the isotopic exchange ratio.

Electrons bombarding the surface of labelled potassium sulphate seems to excite $SO_4{}^{2-}$-ions and individual atoms in the available active centres of the exchange. The electron irradiation affects also gaseous SO_3 activating it; SO_3 and SO_2 ions of different signs are likely to form here. However, the above effect is revealed rather poorly: the exchange rises by some 40% and does not practically change over the dose ranges studied (1.10^{13}-2.10^{13} ev/10 min.).

Radioactive preparations of K_2SO_4 do not undergo any radiation-chemical decomposition which would be accompanied, for example, by the splitting of SO_2 away and by the loss of the corresponding amount of activity. The calcination of the active preparation of $K_2\overset{x}{S}O_4$ in air stream under conditions similar to those of exchange experiments with SO_3 has shown no change either of the weight or of S^{35} contents.

At the same time it should be noted that $K_2\overset{x}{S}O_4$ samples containing S^{35} become violet at the specific activity higher than 1 mc/g. The colour becomes dark-violet when the activity rises up to 20 mc/g. As the S^{35} decomposes and the preparation activity diminishes this colour fades. Almost complete loss of colour of potassium sulphate having the initial specific activity of 16.2 mc/g has been observed after 270 days. The calcination of coloured preparations in air at temperature 800° results in their discolouration. Yet highly active samples recover their colour within several hours.

This phenomenon like the colouring of glass under the effect of irradiation seems to depend upon the displacement of atoms in the crystal lattice and the disturbing of the normal electron repartition in potassium sulphate.

Under the conditions of our experiments the employed addition of sodium sulphate (carrier for S^{35}) had no effect on the ratio of isotopic exchange of sulphur in potassium sulphate. For K_2SO_4 preparation having specific activity of 1.7×10^{-2} mc/g and Na_2SO_4 contents of 0.4%, the isotopic exchange ratio proved to be equal to 11.9% which practically does not differ from the exchange value at the same specific activity but at lower Na_2SO_4 contents (0.04%).

As a result of the radioactive decay of S^{35} Cl^{35} is formed. One might suggest that this element present even in minute amounts brings about the catalytic effect on the process of isotopic exchange of sulphur in $K_2\overset{x}{S}O_4$-SO_3 system. However, on introducing 0.1% KCl into $K_2\overset{x}{S}O_4$ preparation having specific activity of 0.027 mc/g the observed value of the degree of exchange with SO_3 - 11.6% did not differ from that of $K_2\overset{x}{S}O_4$ sample without KCl added. Thus the assumption of the catalytic effect of chlorine on the process of isotopic exchange studied by us is invalid.

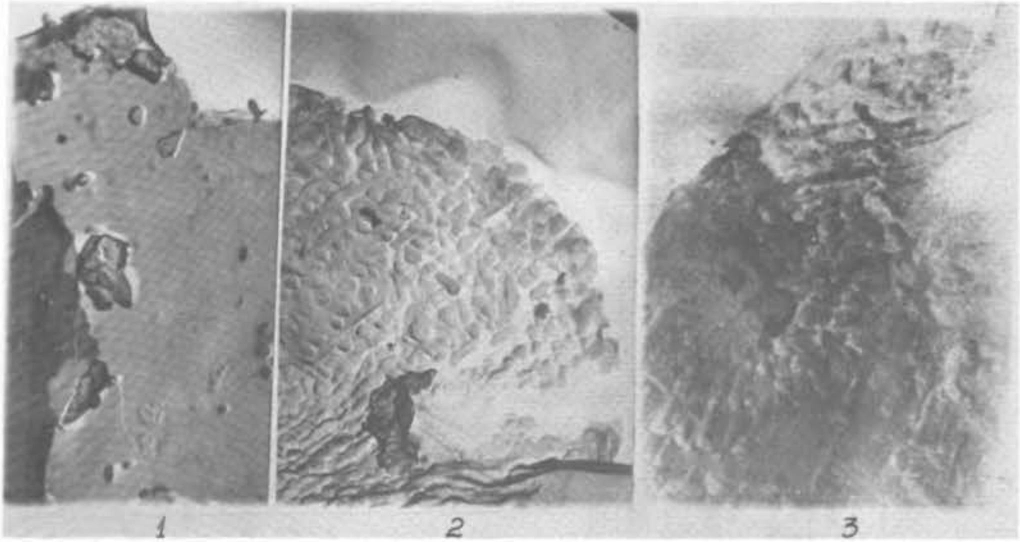
It remains to suppose that β-particles emitted by sulphur-35, when the intensity of their radiation is sufficient, induce the excitation of ions forming K_2SO_4 crystal lattice and particularly SO_4^{2-}-ions. It must contribute to the process of isotopic exchange. An even more important part, perhaps, is played by the appearance of crystal lattice defects, arising in places where the phenomena of radioactive decomposition have taken place. Thus, the thought of the appearance of a great number of active centres at the surface and in the bulk of a solid, because of its radioactivity, suggests itself.

It should be pointed out that the consequences of the above changes remain in potassium sulphate for a long time. $K_2\overset{x}{S}O_4$ radioactive preparations undergoing exposure until their activity was considerably lowered showed nevertheless a high ratio of isotopic exchange with SO_3; this rate did not decrease, but on the contrary, increased as compared with the initial one.

No. preparation	Exposure time in days	Specific activity mc/g		Degree of sulphur exchange %	
		before exposure	after exposure	before exposure	after exposure
1	93	2.0	0.85	65.5	69.4
2	270	16.2	1.9	36.6	78.0

The increase of exchange rate was greater where the initial activity of the preparation was higher and its exposure time greater.

The x-ray investigation carried by us did not show appreciable changes of the crystalline structure of potassium sulphate, in which S^{35} was undergoing decay for a long time, as compared to the ordinary preparations of K_2SO_4. However, by the electron microscope* it was possible to detect that the surface of radioactive potassium sulphate, contrary to non-radioactive preparations, is loose (Fig. 6).



6. Electron-microscopic pictures (x 12,000) of (1) a non-radioactive sample of K_2SO_4, (2) a radioactive sample of $K_2\overset{x}{S}O_4$ freshly prepared (activity, 19 mc/g), and (3) a radioactive sample of $K_2\overset{x}{S}O_4$ stored 753 days (initial activity, 98.8 mc/g), in electronic microscope, 0.25 mc/g.

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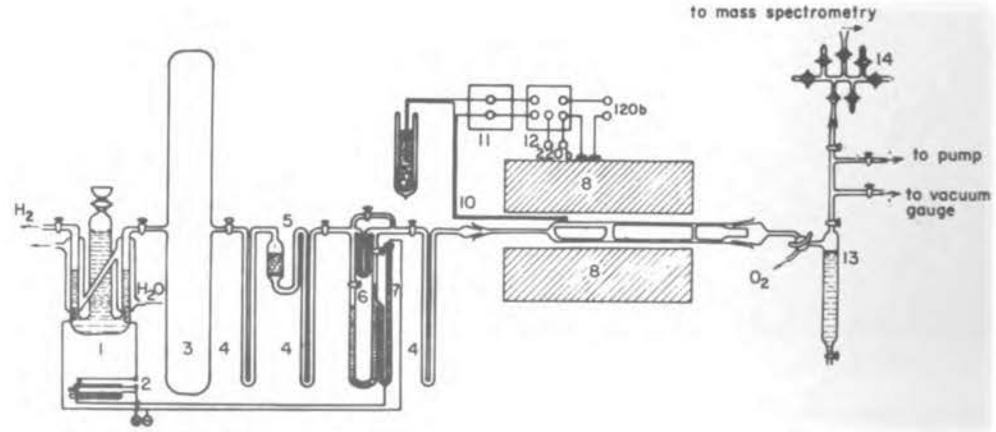
* Electron-microscopic images were taken by L. I. Zemlyanova.

Projections and depressions resembling the corrosion picture are seen on it. Further investigations may be expected to show considerable effect of radioactive radiation of solids on their physical structure.

The radioactive radiation of sulphur-35 has been reported earlier (1) to affect the rate of oxygen isotopic exchange in the $Na_2\overset{x}{S}O_4$-O_2^{18} system too. At present this process has been investigated in more detail (7) for $Na_2\overset{x}{S}O_4$ preparations whose specific activity ranged from 0.08 to 25 mc/g. Gaseous oxygen was labelled with O^{18} (1.3 at.%). The investigation was carried out over the temperature range of 620-790°. The exchange degree was estimated by mass spectrometer. Each experiment lasted 8 hours. The scheme of the apparatus used is given in Fig. 7.

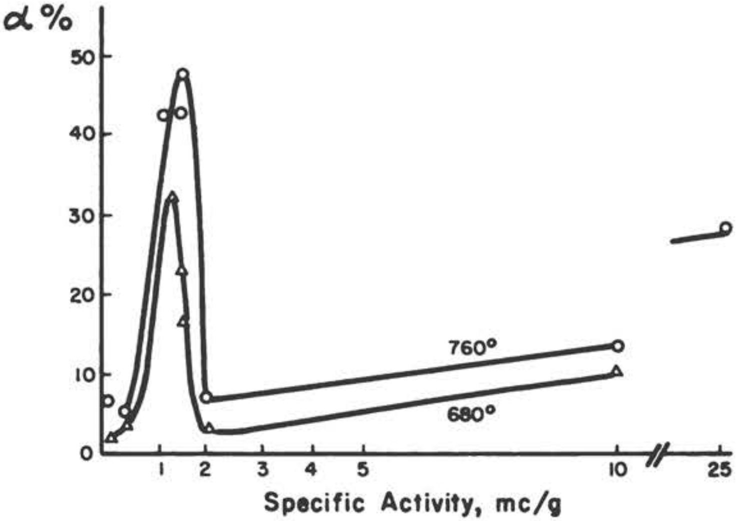


7. The scheme of the apparatus for studying isotopic exchange between gaseous oxygen and Na_2SO_4.
(1) electrolytic cell, (2) relay, (3) capacity cylinder, (4) trap, (5) tube with catalyst, (6) flow meter, (7) sliding contact, (8) electrical furnace, (9) quartz tube with platinum boat, (10) thermocouple, (11) potentiometer, (12) thermocontroller, (13) cylinder for sampling, (14) gas sample receiver.

The technique of the experiments was as follows. Water containing about 1.3 at.% of O^{18}, slightly acidified by addition of H_2SO_4, was electrolyzed in the electrolyzer (1). The oxygen produced was passed through the volumetric cylinder (3), was freed from the traces of hydrogen in the tube with a catalyst (5) and was dried in traps (4) cooled with dry ice and acetone mixture. The velocity of the passage of the gas through the apparatus amounted to 1 ml/min. and was regulated automatically. In the reometer (6) the movable contact (7) was mounted at definite height; when the level of mercury used as a reometric liquid lowered the current in the electrolyzer was switched on by means of the relay and the replenishment of oxygen supply in the volumetric cylinder took place. On raising the mercury level in the reometer tube to an appropriated height electrolysis stopped automatically. The installation operated at mercury pressure 4-5 mm higher than the atmospheric pressure.

The reaction of isotopic exchange took place in the quartz tube (9) heated by the electric furnace (8). The preparations studied were placed in the platinum boat inside the tube. To diminish the volume of the reaction zone quartz pieces were put into the tube. The temperature was measured by means of the thermocouple (10) and the potentiometer (11) and was regulated by the thermoregulator (12). Oxygen passing through the operating tube assembled in the container originally filled with mercury. At fixed intervals oxygen samples were collected in evacuated containers (14) and were taken for mass spectrometer analysis. The remaining oxygen went for regeneration of heavy oxygen water by its interaction with hydrogen. The contents of O^{18} in gas samples was calculated from the relation of peak values of mass 32 and 34 (O_2^{16} and O^{16} O^{18}). The dependence of the isotopic composition of the passing gas upon time was plotted on the basis of the analyses. This allowed to determine the quantity of O^{18} passed into solid phase and hence the degree of exchange. It was found preliminary that the change of isotopic composition of passing oxygen due to its eventual exchange with quartz of the operating tube could be neglected, when the temperature did not exceed 830°.

Fig. 8 shows the dependence of oxygen exchange degree upon the specific radioactivity of $Na_2\overset{x}{S}O_4$ preparations.



8. The dependence of isotopic exchange ratio of oxygen in $Na_2\overset{x}{S}O_4$ - O_2^{18} system on specific activity of $Na_2\overset{x}{S}O_4$.

The observed regularity resembles the picture described for sulphur exchange in the $K_2\overset{x}{S}O_4$-SO_3 system. At temperature

780° the oxygen exchange degree from the non-radioactive preparation of Na_2SO_4 is about 1%. Under the same conditions the preparation of 0.08 mc/g activity exchanges by 7.8%. The maximum exchange is reached at specific activity of $Na_2\overset{x}{S}O_4$ equal to 1.6 mc/g (55.8%). Then the sharp drop of the exchange rate (at 1.9 mc/g - 8.2%) and the slow increase as a result of the further rise of activity (10.3 mc/g - 15.4%; 25 mc/g - 24.3%) can be observed.

One may suppose that in the reaction considered the exchange is accomplished through oxygen which is being absorbed on the surface of solid sulphate.

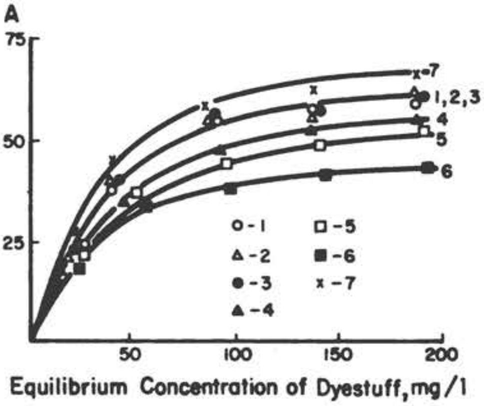
Three branches of the curve in Fig. 8 are likely to arise on the ground of the causes which were discussed for the isotopic exchange in the K_2SO_4-SO_3 system.

Important results were obtained when studying the sorption of some organic dyestuffs from aqueous solutions on the radioactive solid phase (1,3). The change of dyestuff concentration was determined spectrophotometrically. The absence of radiolysis, due to the radioactive radiation, of the dyestuffs employed was controlled during all the experiments. Barium sulphate containing various amounts of sulphur-35 and, in some cases, radium was used as a sorbent.

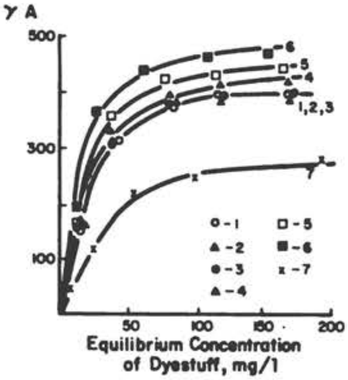
To obtain $BaSO_4$ preparations of constant specific surfaces these were always prepared under standard conditions according to the technique described by Kolthoff (8) and Rutgers (9).

The technique of the experiments was the following: 3 gr. of the precipitate together with 15 ml. of the dyestuff solution of suitable concentration were shaken for 4 hours at temperature $25^\circ \pm 0.5^\circ$. Then the dyestuff contents in the liquid phase was determined spectrophotometrically. The error of the estimation was 3-4%. The period of time necessary for the equilibrium between solid and liquid phases to be reached was established during preliminary experiments. As a rule this period did not exceed 1 hour. The dyestuff concentration varied over the range of 10 to 200-250 mg/l. The solutions were characterized by the following pH values: acid orange - 5.5-5.8, methylene blue - 6.2-6.9.

The investigations have shown that the marked change of barium sulphate sorption capacity is already observed at relatively low specific radioactivity of $BaSO_4$ precipitates i.e. 0.1 mc/g for sulphur-35, 3×10^{-7} mc/g for radium.



9. Sorption (A) of methylene blue (in γ/gr.) by $BaSO_4$ precipitates of various specific activity depending upon the equilibrium concentration of a dyestuff (mg/l). (1) non-active precipitate, (2) precipitate containing 0.01 mc/g S^{35}, (3) precipitate containing 0.1 mc/g S^{35}, (4) precipitate containing 1 mc/g S^{35}, (5) precipitate containing 4 mc/g S^{35}, (6) precipitate containing 10 mc/g S^{35} and (7) $Ba(Ra)SO_4$ precipitate.

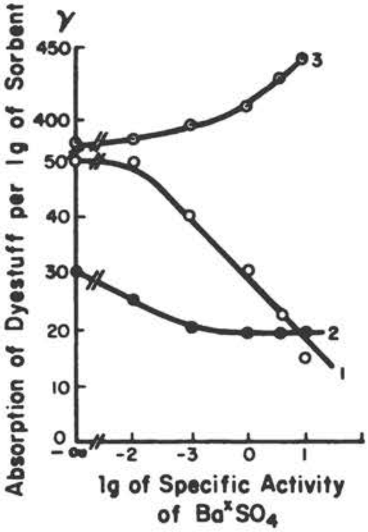


10. Sorption (A) of acid orange (in γ/gr.) by $BaSo_4$ precipitates of various specific activity depending on equilibrium concentration of a dyestuff (in mg/1).
(1) non-active precipitate, (2) precipitate containing 0.01 mc/g S^{35}, (3) precipitate containing 0.1 mc/g S^{35}, (4) precipitate containing 1 mc/g S^{35}, (5) precipitate containing 4 mc/g S^{35}, (6) precipitate containing 10 mc/g S^{35}, and (7) $Ba(Ra)SO_4$ precipitate.

Figures 9 and 10 show the results of sorption measurements of two dyestuffs - methylene blue and acid orange on barium sulphate precipitates of various activity. Introducing S^{35} into $BaSO_4$ preparation leads to the decrease of methylene blue sorption and to the increase of acid orange sorption as compared to the non-radioactive sorbent. The addition of radium has quite an opposite effect.

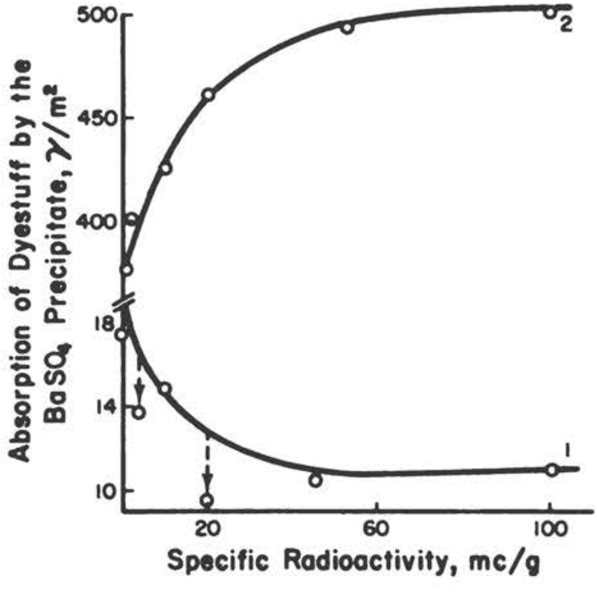
The observed change of the dyestuff sorption may be supposed to be connected with the appearance of the positive charge on the precipitate of radioactive barium sulphate containing S^{35} at the expense of its continuous emission of β-particles and the negative charge on the $Ba(Ra)SO_4$ precipitate due to the emission of α-particles from crystal surfaces. Thus, colored cations must be sorbed worse in the presence of β-radiator and better in the presence of α-radiator. The behaviour of the acid dyestuff in which the anion is colored must be exactly opposite. Experiments with another dyestuff of basic character, brilliant green, have shown that in respect to radioactive sorbents it behaves like methylene blue.

The change of the sorption capacity of $BaSO_4$ precipitates containing S^{35} has been investigated (1,3) over the range of specific activity values of 0.01-10 mc/g. In some cases it occurs proportionately to the logarithm of specific activity of the preparations (Fig. 11).



11. The effect of $Ba\overset{x}{S}O_4$ specific radioactivity on dyestuff sorption. (1) methylene blue, (2) brilliant green, (3) acid orange.

V. I. Spitsyn and V. V. Gromov (1960) extended the investigation of dyestuff sorption to $Ba\overset{x}{S}O_4$ preparations of specific activity up to 101 mc/g. The results proved to be similar to those obtained formerly. The methylene blue sorption decreases still more while the sorption of acid orange increases when highly active samples of barium sulphate have been employed. However, a new phenomenon has been noticed here: the $Ba\overset{x}{S}O_4$ preparations of high activity, allowed to stand for a long time (100-200 days) and reducing their activity respectively, reveal less sorption capacity to methylene blue than freshly prepared samples of the same activity (Fig. 12).



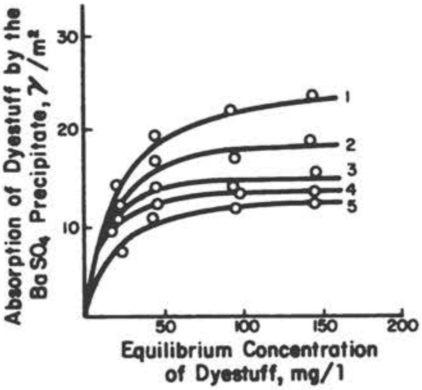
12. Dyestuff sorption by $BaSO_4$ precipitates of high activity. Points marked with dots correspond to samples after standing. (1) methylene blue, (2) acid orange.

Measuring the specific surface of the studied sorbents according to Deryagin's method has shown that it does not undergo any change during the lengthy radioactive decay of S^{35} in $Ba\overset{x}{S}O_4$ preparations. Thus one has to conclude that the standing of highly active barium sulphate samples and very prolonged simultaneous process of β-radiation lead to the decreased number of active centres of adsorption on the sorbent surface without changing the specific surface itself.

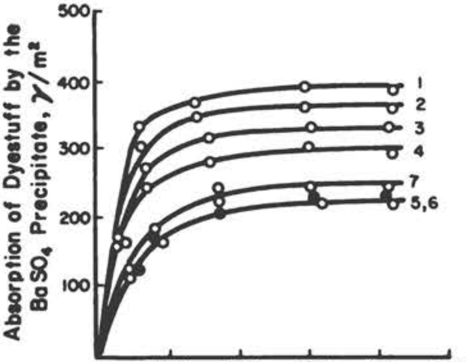
For the acid orange the above phenomenon is not detected so easily because with the decrease of specific activity the $\overset{x}{Ba}SO_4$ sorption of this dyestuff decreases.

The effect of external irradiation on the barium sulphate sorption capacity was studied by the same authors. The initial $BaSO_4$ was calcinated in vacuum at temperature 300-350° in a special metal cylinder. Then it was kept in nitrogen under pressure to prevent the adsorption of oxygen from the air which could form ozone during the irradiation.

The irradiation by electrons, of the energy of 800 Kev was carried out in an aluminum cuvette with water cooling, nitrogen being blown through. Temperature was kept over the range of 15-30°. In addition, the irradiation by protons of 1.5 Mev energy was investigated; these protons were produced by the electrostatic generator of Van-de-Graaff type. These experiments were run in vacuum (10^{-5}-10^{-6} mm of Hg.). In spite of the water cooling of the target the preparation was heated up to 100-150°. After the irradiation by protons the induced activity was not detected. The sorption capacity of irradiated and non-irradiated $BaSO_4$ preparations was studied simultaneously. The results obtained are shown in Figs. 13 and 14.



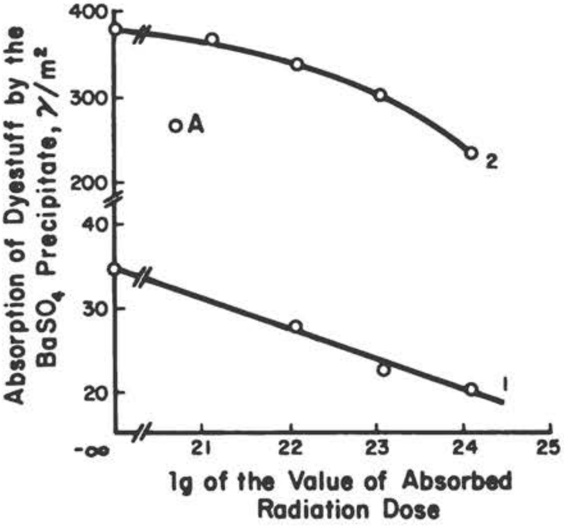
13. Sorption of methylene blue by $BaSO_4$ precipitates irradiated by electrons of high energy. (1) non-irradiated sample; samples having absorbed an integral irradiation dose: (2) 1.3 x 10^{22} ev/gr., (3) 1.3 x 10^{23} ev/gr., (4) 1.3 x 10^{24} ev/gr., (5) 1.3 x 10^{23} ev/gr. (at less intensive dose).



14. Sorption of acid orange by $BaSO_4$ precipitates irradiated by electrons of high energy and by protons. (1) non-irradiated sample; samples having absorbed an integral irradiation dose by electrons: (2) 1.3 x 10^{21} ev/gr., (3) 1.3 x 10^{22} ev/gr., (4) 1.3 x 10^{23} ev/gr., (5) 1.3 x 10^{24} ev/gr., (6) 1.3 x 10^{23} ev/gr. (at less intensive dose; (7) sample having absorbed an integral irradiation dose by protons, 0.4 x 10^{21} ev/gr.

As the absorbed integral dose of the electron irradiation increases the sorption of both dyestuffs studied - methylene blue and acid orange - decreases considerably. It is of interest to note that when the magnitude of the dose employed has been diminished and at the same time the treatment time has been increased prolonged a considerable drop of BaSO$_4$ sorption capacity can be achieved using the lesser dose of integral irradiation.

The bombardment of barium sulphate by protons causes much sharper drop of its sorption capacity than the irradiation by electrons, the magnitude of the dose being the same. The decrease of the dyestuff adsorption by the irradiated BaSO$_4$ preparations occurs almost directly proportionate to the magnitude of the dose of the absorbed radiation (Fig. 15).

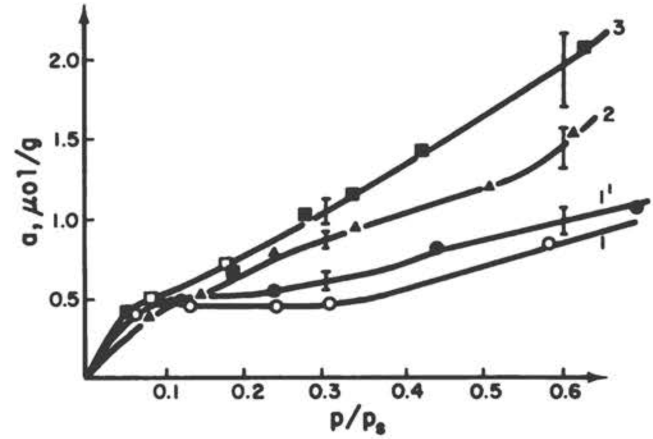


15. Dyestuff sorption by barium sulphate depending on the absorbed dose from external electron irradiation. (1) methylene blue, (2) acid orange. Point A corresponds to the preparation irradiated by protons.

$BaSO_4$ preparations subjected to the electron or proton irradiation do not undergo marked chemical decay. One observes the appearance of light greyish-brown colouration which disappears in a week yet sorption properties are not recovered even in 20-25 days. On calcinating within 1 hour at 200-250° the colouration disappears and the sorption properties of the irradiated samples are almost completely recovered.

The measurements of the specific surface of $BaSO_4$ preparations have shown that it is not changed when irradiated. Thus the treatment of barium sulphate by particles of high energy - electrons and protons - exerts peculiar "polishing" effect which seems to cause the decrease, on the surfaces of irradiated preparations, of the number of active centres determining sorption properties. The above facts should be kept in mind when trying to obtain active solids by irradiation methods.

At present first evidence of the effect of the sorbent radioactive radiation on the adsorption processes of gaseous substances was obtained. The experiments were made using finely powdered K_2SO_4 preparations containing S^{35}. The adsorption of methanol vapours was measured by means of the apparatus described in (11). The results are shown in Fig. 16.

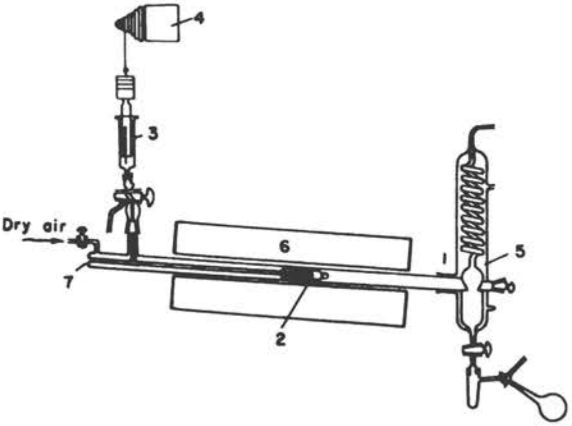


16. Adsorption of methanol vapours on radioactive and non-radioactive samples of K_2SO_4 (25°). (1, 1') non-radioactive K_2SO_4 preparations, (2) radioactive preparation of $K_2\overset{x}{S}O_4$ (17.2 mc/g) after standing for 30 days, (3) radioactive preparation of $K_2\overset{x}{S}O_4$ (0.08 mc/g) after standing for 473 days. Black dots correspond to samples evacuated before the experiment at 200°, the rest - to samples evacuated at 20°.

The methanol adsorption by the $K_2\overset{x}{S}O_4$ sample having the specific activity of 17.2 mc/g turned out to be 20% higher than in the case of a non-radioactive preparation. The $K_2\overset{x}{S}O_4$ sample of specific activity of 0.08 mc/g, in which β-decay continued for about 500 days, had the sorption capacity 40% higher than the non-radioactive K_2SO_4. Hence, not only the real activity of the studied sorbent but the duration of its stay under the conditions of radioactive decay is of importance. It should be recalled that the analogous phenomenon, i.e. the accumulation of the effect of irradiation, was observed for the isotopic exchange in the K_2SO_4-SO_3 system.

The effect of introducing various quantities of radioactive isotopes into the catalysts of heterogeneous reactions was mainly studied by means of dehydration processes of alcohols, chiefly of cyclohexanol. The reaction rate of cyclohexanol dehydration was determined (4) over the temperature range of 335-415° using a catalyst consisting of a mixture of $MgSO_4$ and $NaSO_4$. Various quantities of sulphur-35 in the form of radioactive sodium sulphate were introduced into the catalyst. Every time cyclohexene yield was compared for two catalysts of the same composition, one of them contained S^{35}, the other being non-radioactive.

The investigation was carried out in catalytic apparatus of through streamed type (Fig. 17) described in (12). The catalytic tube (1) with an inserted reactor, (2), ground to its inner surface, were made of quartz. Cyclohexanol was uniformly supplied into the catalytic tube at the rate of 0.22 ml/min. out of an injector, (3), connected with a special device for



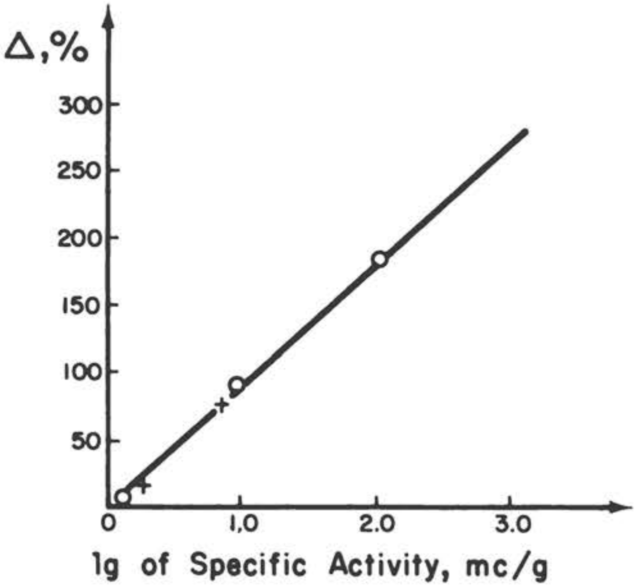
17. The scheme of the apparatus for carrying catalytic experiments.

automatic liquid supply (4). From outside, the syringe was heated by an external jacket thermostated at 30°, for at room temperature cyclohexanol hardens. In all the experiments into the reactor (2) was fed 0.5 ml of each of the prepared catalysts whose weights ranged from 0.16 to 0.30 g. Volumetric supply rate was 0.4 min^{-1}. Reaction products were condensed in the receiver (5) with coil cooler made of molybdenum glass. (Fig. 17).

Each experiment lasted 30 minutes and the catalysate collected during the first 15 minutes was discarded. The extent of cyclohexanol transformation was determined by titrating, after Kaufman bromine method, the catalysate sample obtained during the second 15 minutes after the beginning of the experiment.

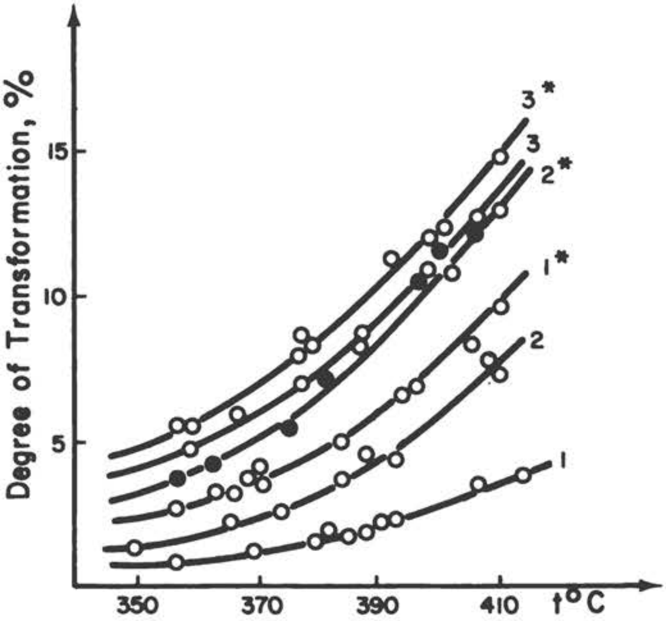
The catalytic tube was heated by an electric tubular furnace (6) with a dilatometric thermoregulator. The accuracy of maintaining constant temperature was ± 2°. The temperature in the reaction zone was measured by a chromelalumel thermocouple placed into the quartz pocket (7) going deeply into the inserted reactor (2) containing the catalyst. After each experiment the catalyst was regenerated for 45 minutes by a stream of dry air passing at the rate of 9 l/hr. In the apparatus behind the receiver with the catalysate (5) was an intensimeter of labelled atoms intended for determining soft beta-radiation. The formation of gaseous reactions products which would contain S^{35} was never observed. In the catalysate, as a rule, no radioactivity was found except the cases of its mechanical contamination with the catalyst chanced to be powdered.

Passing to the experimental results one may note that at temperature 410°, the catalyst specific activity being 1.26 mc/g, the extent of cyclohexanol transformation increases by 10%; at 9.2 mc/g - by 90% and at 105.2 mc/g - by 180%. The increase of the extent of cyclohexanol transformation takes place in proportion to the logarithm of catalyst specific activity (Fig. 18).



18. The dependence of increasing the extent of cyclohexanol transformation on the catalyst specific radioactivity. Crosses refer to the catalyst having the initial activity 105.2 mc/g after its standing for 188 and 314 days respectively.

The results of determining the extent of cyclohexanol transformation with catalysts of various compositions at various temperatures are presented in Fig. 19. In all cases the curve corresponding to the radioactive catalyst lies higher than the one corresponding to the non-radioactive catalyst.



19. The effect of catalyst radioactivity on its catalytic activity.

1. $MgSO_4$ + 21.87% Na_2SO_4 (non-radioactive);
1*. $MgSO_4$ + 21.87% Na_2SO_4 (activity-105.2 mc/g);
2. $MgSO_4$ + 4.06% Na_2SO_4 (non-radioactive);
2*. $MgSO_4$ + 4.06% Na_2SO_4 (activity-9.2 mc/g);
3. $MgSO_4$ + 0.52% Na_2SO_4 (non-radioactive);
3*. $MgSO_4$ + 0.52% Na_2SO_4 (activity-1.26 mc/g).

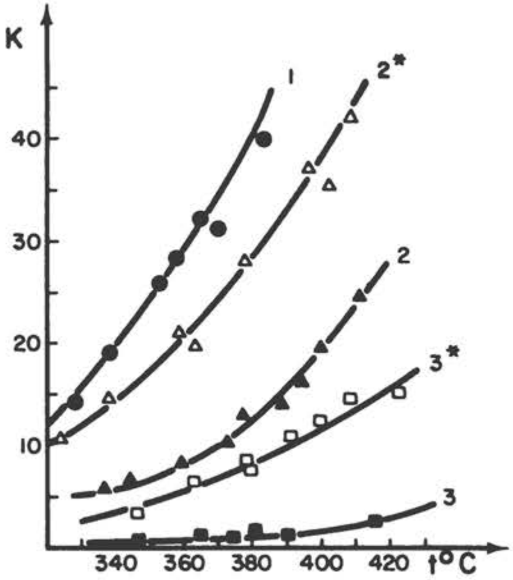
Calculations show that apparent activation energies of the catalytic process studied decrease slightly (by 1-2 Kcal/mole), but definitely, when the radioactive isotope, S^{35}, is introduced into the catalyst.

Hence, that the radioactive radiation of a catalyst at sufficient intensity affects its catalytic activity and the activation energy of the process should be considered as established. The mechanism of increasing the catalytic activity seems to be connected with the increase of the number of active centres due to the appearance of defects in the crystalline lattice and on the surface of a catalyst and it appears also to depend upon beta-radiation effect on catalytic active centres adsorbing molecules of a reacting substance.

Further investigations (13) have shown that as S^{35}, which is a constituent of a catalyst for cyclohexanol dehydration (the $MgSO_4$ and Na_2SO_4 mixture), decays, its catalytic activity decreases in accordance with the regularity described earlier (4) (Fig. 18).

This observation allows to discard the supposition that chlorine formed during the decay of sulphur-35 plays any part in the increased catalytic activity of radioactive magnesium sulphate. On the other hand, the opinion stated formerly (4) is confirmed that the very β-radiation of a radioactive catalyst is the cause of its increased catalytic activity.

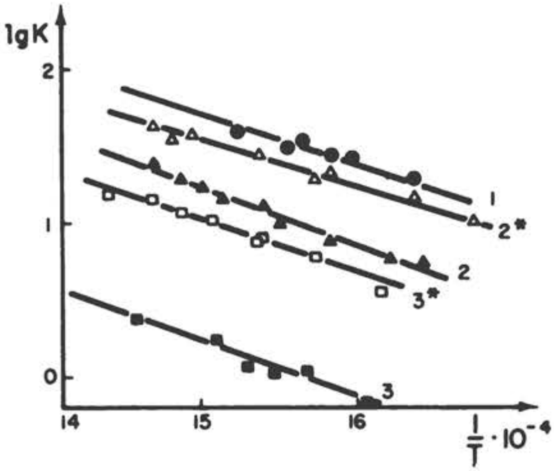
It was found that instead of sulphur-35 into the magnesium sulphate may be introduced a different radioactive isotope which is not a catalyst constituent and that it increases its catalytic activity. Thus, for instance, calcium chloride is not a catalyst of the reaction of cyclohexanol dehydration. The addition of $CaCl_2$ to magnesium sulphate is the cause of a great decrease of the extent of cyclohexanol transformation. However the presence of a radioisotope, Ca^{45}, in $CaCl_2$ changes the picture (Fig. 20).



20. The effect of addition of non-radioactive and radioactive $CaCl_2$ on catalytic activity of $MgSO_4$ in cyclohexanol dehydration reaction.

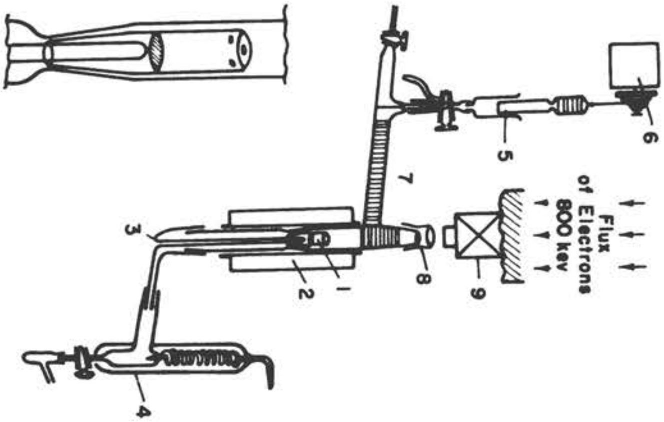
1. $MgSO_4$
2. $MgSO_4$ + 13.82% $CaCl_2$ (non-radioactive)
2.* $MgSO_4$ + 13.93% $CaCl_2$ (activity-12 mc/g).
3. $MgSO_4$ + 49.87% $CaCl_2$ (non-radioactive).
3.* $MgSO_4$ + 49.82% $CaCl_2$ (activity-45.1 mc/g).

It may be pointed out that the activation energy of the cyclohexanol dehydration process decreases markedly (by 1-4 Kcal/mole) when radioactive $CaCl_2$ is added to magnesium sulphate (Fig. 21).



21. The dependence of the constant of the reaction rate of cyclohexanol dehydration on reverse temperature (catalysts - $MgSO_4$ or mixtures $MgSO_4$ and $CaCl_2$). The catalyst designations are the same as in Fig. 20.

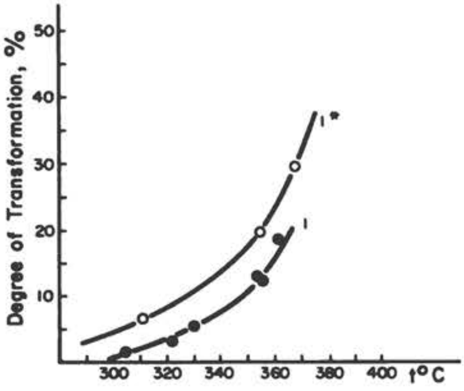
Special experiments were made (13) using the external irradiation of magnesium sulphate and cyclohexanol vapours by electrons of high energy in the course of dehydration reaction for comparison with the action of radioactive catalysts. The scheme of the corresponding apparatus is shown in Fig. 22.



22. The scheme of the apparatus for irradiating catalyst by electrons of high energy in the course of reaction. (1) reactor with catalyst (on the left hand side - the magnified picture of the reactor), (2) electric furnace, (3) quartz pocket for thermocouple, (4) receiver for catalysate, (5) syringe for supplying cyclohexanol, (6) automatic device to the feeder, (7) evaporator, (8) membrane of molybdenum glass 100 μ thick, (9) ionisation chamber of electron accelerator.

The investigation has shown that the employing of electrons of energy 800 Kev. did not lead to any acceleration of the process. Thus, in this case, too, the radioactive radiation of a solid turns out to be more effective than its external irradiation.

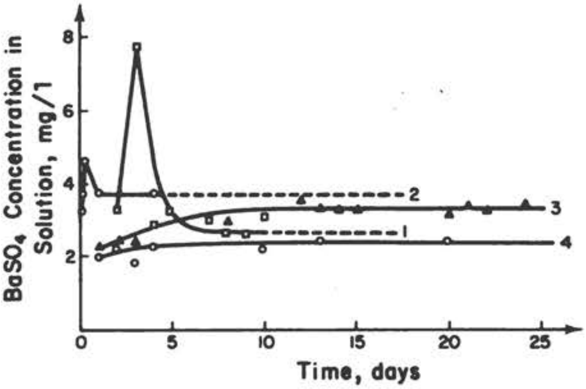
Good results were obtained when using new radioactive catalysts. I. E. Mickhailenko and N. P. Dobroselskaya (1960) studied the dehydration of n-dodecyl alcohol on tribasic calcium phosphate. The introduction of radioactive phosphorus, P^{32}, into the catalyst allowed, at the specific activity of the preparation equal to 27.6 mc/g, to observe a marked acceleration of the process. (Fig. 23).



23. The effect of radioactivity of tribasic calcium phosphate catalyst on the kinetics of n-dodecyl alcohol dehydration.
(1) non-radioactive catalyst, (1^*) radioactive catalyst containing P^{32} (27 mc/g).

One of the first applications of the method of labelled atoms was to use radioactive isotopes for estimating the solubility of non-soluble substances. In the light of new data obtained about the effect of the radioactive radiation of solids on the heterogeneous processes proceeding with their participation one might think that the presence of irradiators should affect the nature of the interaction of a solid phase and a saturated solution when dealing with scarcely soluble compounds.

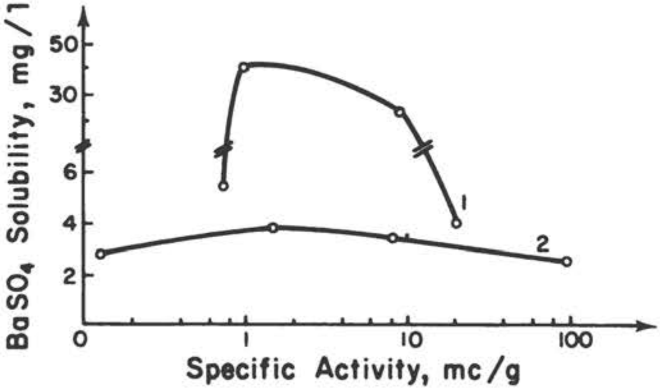
V. I. Spitsyn, E. A. Torchenkova and I. N. Glaskova (14) have investigated the kinetics of the dissolution process, in water, barium sulphate containing various amounts of S^{35}. At the specific radioactivity of preparations of the order of 0.1-1.5 mc/g one observes at first considerable over-saturation of solutions which is eliminated after approximately 25 hours of agitating of the liquid with the precipitate. The $BaSO_4$ precipitations of higher activity (9-20 mc/g and higher) do not reveal similar phenomenon: the $Ba\overset{x}{S}O_4$ concentration in these precipitates increases with time (Fig. 24).



24. Kinetics of dissolving, in water at 20°, preparations of various specific activity.
(1) 0.7 mc/g, (2) 1.0 mc/g, (3) 9.0 mc/g, (4) 19.9 mc/g.
The salt was prepared by pouring together equivalent amounts of 0.1 N $BaCl_2$ and $Na_2\overset{x}{S}O_4$ solutions.

The dissolution kinetics of $Ba\overset{x}{S}O_4$ precipitate depends on the method of its preparation. If the initial substance was radioactive sodium sulphate, the transfer of SO_4^{2-}-ions into the solution is accomplished faster and on attaining equilibrium the calculated solubility of $BaSO_4$ (20-40 mg./l, 20°)

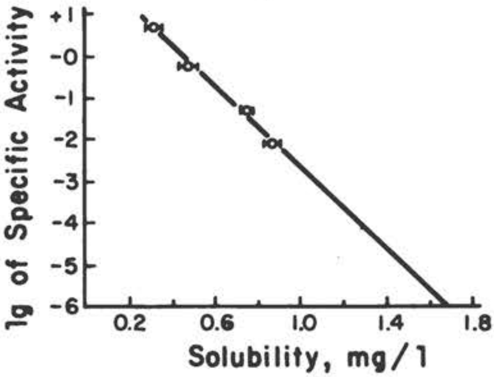
considerably increases the value known for barium sulphate (2.3 mg./1, 18°). If precipitates are prepared proceeding from labelled sulphuric acid, the $BaSO_4$ solubility measured by the concentration of SO_4^{2-}-ions turns out to be much lower (4-6 mg/1, 20°) although it exceeds the solubility of non-radioactive barium sulphate. It is interesting to note that in both cases the observed solubility of barium sulphate containing various quantities of S^{35} has its maximum at specific radioactivity of preparations of order 1-1.5 mc/g (Fig. 25).



25. The effect of $Ba\overset{x}{S}O_4$ specific activity on the value of its solubility in water at 20°. The means of obtaining $Ba\overset{x}{S}O_4$: (1) $BaCl_2 + Na_2\overset{x}{S}O_4$, (2) $BaCl_2 + H_2\overset{x}{S}O_4$.

One should conclude that the process of dissolving the solid phase containing considerable quantity of a radioactive isotope is rather complicated and, perhaps, connected with the change of the electro-kinetic potential of the precipitate owing to the appearance of charges on its surface due to the continuous radioactive radiation.

Measuring solubility of cerium(III) oxalate labelled by various quantities of Ce^{144} ($T_{1/2}$ = 282 days) (15) may be stated as another example studied. Four samples of cerium oxalate of the following specific radioactivity: 0.008, 0.05, 0.5 and 4.3 mc/g were prepared under identical conditions. The results of the investigation have shown that alongside with the increase of the specific activity of cerium oxalate its solubility, determined according to the Ce^{144} indicator, decreases. The composition of the bottom phase is practically not changed. The cerium oxalate solubility is shown by Fig. 26 to be linearly dependent upon the logarithm of the specific activity of preparations. Extrapolating the straight line along the axis of abscissa for the infinitesimal activity of a precipitate gives the value of cerium oxalate solubility which is quite close to the value found by ordinary methods, i.e. by weight and volumetrically.



26. The solubility, in water, of cerium oxalate of various specific activity. Temperature 25°.

The sharper effect of radioactive isotope on the cerium oxalate solubility, as compared with $BaSO_4$ obviously, may be accounted for by the high radiation energy of Ce^{144} (E_{max} = 0.348 Mev.) and the filial shortlived Pr^{144} (E_{max} = 2.97 Mev.; $T_{1/2}$ = 17.5 min.).

Hence, the radiation effect of the employed radioactive indicator on the solubility value of weakly soluble compounds must be taken into account when using the method of labelled atoms.

New experimental data reported in the present paper show the important effect of radioactivity of solids on heterogeneous processes in which they take part. One may be sure that further investigations will enlarge the sphere of phenomena in which the radioactive radiation may affect physico-chemical properties of various substances. The use of radioactive isotopes, without doubt, will allow to develop and perfect the methods of preparation of active solid bodies having important applications in research and modern engineering.

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RECENT ADVANCES OF RADIOCHEMISTRY IN THE USSR

by V. I. Spitsyn

Extensive development of research in radiochemistry all over the world is stimulated by the steadily growing use of atomic power, by the rapidly increasing production of fissionable materials and by the successful application of radioactive isotopes in different fields of science and technology.

In this country a vast program for the construction of electric stations on atomic power is being carried into effect. According to the seven-year plan for development of the national economy in 1959-1965 the industrial use of atomic energy is to be extended considerably. The chemistry of radioactive elements has been an intensively studied field, too.

In fact, the investigation of radioactive substances has been a tradition with Russian science. It was begun soon after the discovery of radioactive phenomena and received special impetus in the forties of this century, when the new practical possibilities opened up by the fission of uranium became evident.

Early in 1958 the author of this paper had the privilege of reporting to the American Atomic Congress in Chicago on the status of radiochemical research in the USSR (1). The present review contains information about the most important results of Soviet work on radiochemistry carried out in 1958-1960.

Cocrystallization and adsorption remain very important processes when radioactive elements are isolated from dilute solutions.

As established by Khlopin and his school (2, 3, 4), the distribution of microscopic quantities of an isomorphous substance between the solid crystalline and liquid phases obeys the following law:

$$\frac{x}{(1 - x)} \cdot \frac{(1 - y)}{y} = D,$$

where x and $(1 - x)$ are microcomponent ratios in the solid and liquid medium; y and $(1 - y)$ are the respective macrocomponent ratios; D is the fractionation coefficient. In other words, van't Hoff's theory for dilute solutions is applicable to the case where isomorphous mixtures representing dilute solid solutions are formed. In this case the distribution of an electrolyte in a state of extreme dilution between the solid crystalline phase and the liquid phase is analogous to the distribution of a dissolved substance between two immiscible liquid solvents, which is known to obey the Berthelot-Nernst law.

The fractionation coefficient, D, is a constant quantity, independent of either the microcomponent concentration in the solution or the amount of solid phase liberated from the latter, provided that the precipitate and the solution are in equilibrium and that the chemical compounds present in the liquid and solid phases have the same composition.

What has been just stated here has been confirmed by a thorough study of more than 30 systems of true isomorphous substances, viz., $BaCl_2$-$RaCl_2$-H_2O; $Ba(NO_3)_2$-$Ra(NO_3)_2$-H_2O; $Ba(NO_3)_2$-$Ra(NO_3)_2$-HNO_3-H_2O; $BaCrO_4$-$RaCrO_4$-H_2O; $U(SO_4)_2$-$UX_1(SO_4)_2$-H_2SO_4-H_2O; Na_2Te-Na_2Po-H_2O and others.

For the isomorphism of the second kind (Grimm's mixed crystals) the lower limit of miscibility has been established: the microcomponent begins entering the macrocomponent crystals if its concentration attains a certain minimum (above 10^{-5} - 10^{-6}%) sufficient for the microcomponent to build its own crystal lattice. In this case the isolated crystals have a mosaic structure. The existence of a lower miscibility limit has been borne out by the results obtained in investigating a number of systems, viz., $KClO_4$-$RaSO_4$; $KClO_4$-$Pb(RaD)SO_4$; $KMnO_4$-$RaSO_4$, and others.

For anomalous mixed crystals too the lower miscibility limit has been stated in several different instances, viz., systems NH_4Cl-$FeCl_3$-H_2O; NH_4Cl-$MnCl_2$-H_2O; $Ba(NO_3)_2$-methylene blue; and others. It has been found that with certain microcomponent concentrations a true stable equilibrium between these crystals and the solution is possible, in accordance with Khlopin's law (5).

Khlopin's investigations have shown that in the case of isomorphous substitutions crystals become homogeneous through a long recrystallization of the precipitate in the saturated solution and also when the crystals of macrocomponent are precipitated from a supersaturated solution by rapid mechanical stirring.

It is well to note that the latter technique (the isothermal breakdown of supersaturation) led in several experiments of different authors to a non-homogeneous distribution of the microcomponent in crystal layers, obeying Doerner-Hoskins's logarithmic law (6):

$$\ln \frac{a}{a - x} \bigg/ \ln \frac{b}{b - y} = \lambda$$

where a and b are the amounts of macro- and microcomponent in solution before the liberation of the solid phase; (a - x) and (b - y) are the respective amounts after liberation; λ is the fractionation coefficient.

The work done by Khlopin and collaborators was of great value in principle, but the mechanism underlying the formation of anomalous mixed crystals was not brought to light and the application of the distribution law to systems containing crystals of mosaic structure was rather formal. The nature of the internal adsorption systems described by Hahn (7) was not explained either.

Soviet radiochemists have done much to develop research on the line initiated by Khlopin. In recent years they have secured abundant experimental evidence in support of his conclusions. From these data it is evident at the same time that in the case of anomalous mixed crystals and internal adsorption systems cocrystallization phenomena are a matter of great complexity.

Grebenschikova and collaborators (8) have shown that on isothermal breakdown of supersaturation in solutions the distribution of the microcomponent can follow both Khlopin's linear law and the logarithmic formula of Doerner-Hoskins. Under constant conditions of experiments the behavior of the microcomponent depends on the solubility of the precipitate, on its ability to give supersaturated solutions, on the relative rate of crystal growth and on other factors. To take the system K_2SO_4-$Ce_2(SO_4)_3$-HNO_3-H_2O as an example, a very good coincidence with Khlopin's law was observed (D = const) when HNO_3 was a 1.5 N solution, whereas with an 0.5 N solution of HNO_3 Doerner-Hoskins's law was followed (λ = const). The solubility of the double salt precipitate is considerably higher in 1.5 N HNO_3 than in 0.5 N HNO_3, which makes its recrystallization easier.

In studying the coprecipitation of Am^{3+}, La^{3+} and Ce^{3+} with K_2SO_4 it was found that anomalous mixed crystals having no lower solubility limit are formed in the K_2SO_4-$La_2(SO_4)_3$-0.5 N HNO_3, K_2SO_4-$Ce_2(SO_4)_3$-0.5 N HNO_3 and K_2SO_4-$Am_2(SO_4)_3$-0.5 N HNO_3 systems. La^{3+}, Ce^{3+} and Am^{3+} are distributed within the K_2SO_4 crystals according to a logarithmic law with constant λ values, which are distinct for each of the microcomponents, viz., $\lambda_{Ce} = 15$, $\lambda_{La} = 17$ and $\lambda_{Am} = 42$. These values of λ do not change when the respective elements are present together. Foreign ions (Fe^{3+}, Al^{3+}, Bi^{3+}) have no effect on the value of the fractionation coefficients found, and so the formation of internal adsorption systems is here impossible.

For systems with a lanthanum salt, $La_2(C_2O_4)_3 \cdot 9H_2O$ or $K_3La(SO_4)_3$, as a macrocomponent and with Y^{3+}, Eu^{3+}, Am^{3+} and Pu^{4+} as microcomponents Khlopin's law was observed and the lower miscibility limit was absent. Especially interesting is the fact that tetravalent plutonium enters into the lattice of lanthanum salts to form, in spite of the difference in valence, ordinary mixed crystals instead of anomalous. Its concentration varied from 2×10^{-3} to 7×10^{-7} M in the case of the double potassium lanthanum sulphate as macrocomponent and from 4×10^{-6} to 5×10^{-9} M in the case of lanthanum oxalate.

Essential also is that all of the multivalent ions investigated (trivalent - Y^{91}, La^{140}, Ce^{141}, Am^{241}; tetravalent - Zr^{95} and Pu^{239}) are captured by the K_2SO_4 crystal lattice without a lower miscibility limit. It has been suggested by the cited authors that the microcomponents mentioned enter into the potassium sulphate lattice in the form of double salts, which are formed at the surface of K_2SO_4. Also the penetration of Pu^{4+} into the $K_3La(SO_4)_3$ lattice is explained by the formation of a complex ion $[Pu(SO_4)_3]^{2-}$ in the sulphate solution, this ion being able to replace the $[La(SO_4)_3]^{3-}$ ions whereby an anion is introduced into the interstitial space to compensate the charge. Increase or decrease in the K_2SO_4 concentration in solution brings about a reduction of the fractionation coefficient of the $[Pu(SO_4)_3]^{2-}$ ion. It has been proposed that the instability constants, $K_{in.}$ of complex ions formed by the microcomponent should be computed from the observed values of the fractionation coefficients. Thus, for the oxalate complex Pu^{4+}-$[Pu(C_2O_4)]^{2+}$ the following formula was used:

$$K_{in.} = \frac{\left[C_2O_4^{\,2-}\right]}{\left[\frac{D_f}{D_o} - 1\right]}$$

Here D_f is the fractionation coefficient in the presence of complex formation; D_o is the fractionation coefficient when no complex is formed. The value of $K_{in.}$ was found to be $5.2 \times 10^{-7} \pm 10\%$.

E. M. Ioffe (9) has arrived at a similar conclusion. According to her, the formation of anomalous mixed crystals, in some cases at least, is due to the structural analogy between the macrocomponent and the complex salts formed by it with the microcomponent rather than to the crystallographic similarity of the initial substances, as observed in the case of a true isomorphism.

She experimented with systems consisting of NH_4Cl and chlorides of Fe^{3+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, and Co^{2+}, and with some organic systems containing inorganic elements. Of the nine systems she investigated six undoubtedly had a lower limit for the formation of mixed crystals (D was observed to decrease sharply with decreasing microcomponent concentration in solution). For the NH_4Cl-$CuCl_2$ and NH_4Cl-$MnCl_2$ systems the fractionation coefficient remains invariable within a wide range of concentration. In this case the complex ion $[MnCl_4.2H_2O]^{2-}$ seems to replace the 2 $NH_4^+.4Cl^-$ groups in the NH_4Cl lattice. In the systems containing iron or chromium chlorides the complex ions $[FeCl_5.H_2O]^{2-}$ and $[CrCl_5.N_2O]^{2-}$ are present, which are incapable of the substitution just mentioned.

Similar results have been obtained with systems containing two microcomponents each, viz., with NH_4Cl-$MnCl_2$-$CuCl_2$-H_2O and NH_4Cl-$FeCl_3$-$CrCl_3$-H_2O. Here manganese and copper retain the values of their distribution coefficients. The distribution coefficient of chromium is somewhat higher in the presence of iron. The reason for this, as suggested by that author, is that during the precipitation of crystals the complex anion $[CrCl_5.H_2O]^{2-}$ is deposited on the ready portions of the lattice which are formed by the complex anion $[FeCl_5.H_2O]^{2-}$ isomorphous with them.

M. S. Merkulova and collaborators have investigated the coprecipitation of divalent metal ions with salts forming crystals of sodium chloride structure. The systems studied were NH_4I-PbI_2, $NaCl$-$PbCl_2$, $NaCl$-$SrCl_2$ and $NaCl$-$CdCl_2$. It has been found that the microcomponents are slow to come to equilibrium in these systems. This corresponds to the mechanism of solid solution formation. The distribution of the Pb^{2+}, Sr^{2+} and Cd^{2+} ions in the volume of solid phase is uniform, as shown by the fact that the fractionation coefficient D is constant for a given concentration of the distributed substance. On the strength of the experimental data obtained it is suggested that solid solutions of limited miscibility are formed by microscopic quantities of $PbCl_2$, $SrCl_2$ and $CdCl_2$ with NaCl crystals (10).

The results obtained in experimenting upon the joint coprecipitation of microscopic quantities of both Pb and Bi with NaCl were used for a quantitative separation of lead and bismuth isotopes. Those experiments had shown that microquantities of $PbCl_2$ and $BiCl_3$ were distributed between the crystals and the saturated solution of sodium chloride independently of each other, each having its own distribution coefficient. The absolute values of fractionation coefficient are strikingly different: $D_{Pb} = 200$, $D_{Bi} = 0.5$. By a twofold precipitation of sodium chloride from a supersaturated solution containing RaD and RaE the lead and bismuth isotopes can be separated completely (11). The same authors used non-isomorphous systems $NaCl\text{-}PbCl_2\text{-}H_2O$ and $NaCl\text{-}CdCl_2\text{-}H_2O$ for a thorough study of the mechanism underlying the formation of limited solid solutions. To that purpose they investigated the dependence of the microcomponent concentration in the solid phase upon the overall concentration of the impurity in the system. An upper miscibility limit was observed in these systems, and a Langmuir type of equation (12) was found to describe the variation of the impurity concentration in the solid phase as a function of its overall concentration in the system.

Subjected to a theoretical discussion was the formation of solid substitution solutions at the main crystallization stages, viz., when the crystallization centres (nuclei) are forming and during crystal growth. These theoretical considerations were checked by experiment. To reveal the coprecipitation regularities during nucleation of the crystals the fluctuation theory was resorted to. It has been shown that no equilibrium is established when the radioelement is being distributed between the nuclei and the supersaturated solution in which they are forming. The concentration of the radioelement in the volume of the nuclei is close to its concentration in the initial solution. On modern crystallization concepts it has been established that the impurity can be so distributed as to be either in or out of equilibrium depending on the conditions of crystallization: the solubility, surface energy and density of the macrocomponent crystals, the mode and rate of nucleation, the temperature, etc. By adjusting suitably these factors the recrystallization of the solid phase can be repeated many times during an experiment, and the distribution coefficient D in equilibrium can easily be determined. On the other hand, the conditions of crystallization can be so chosen that there will be no recrystallization during the experiment. In the latter case the regularities in the coprecipitation of microimpurity with the growing macrocomponent crystals can be studied (13).

Investigated by experiment was the formation of the solid macrocomponent phase on the precipitation of NaCl crystals from a slightly supersaturated solution when it is being stirred. It has been found in these experiments that accumulation of the radioelement in the precipitate takes place when a constant number of nuclei of critical size are in progress of growth. In studying the phenomena taking place at the surface of a growing submicron a quasicrystalline model of liquid was used. The radioelement coprecipitation mechanism was considered at a stage of dynamic adsorption exchange between the crystal surface and the solution and at a stage, when a new monomolecular layer is being regularly deposited on the surface of the crystals of carrier. The main relations were deduced which govern the transition of the impurity to the surface layer and the distribution of the radioelement in the volume of the carrier crystals under different conditions of crystallization. The theoretical regularities were borne out by experiments with several different systems, viz., $NaCl-PbCl_2$, $NaCl-CdCl_2$, NaCl-TlCl and $NaCl-InCl_3$ (14).

Theoretical investigations on the distribution of ions between the solid and liquid phases and on the kinetics of the process by which the respective equilibria are attained have been made by Kirgintsev (15). His thermodynamic calculations have revealed a profound analogy between the cocrystallization and adsorption phenomena. He obtained for the coprecipitation isotherm the equation

$$K_x^m = b(Z_1 - \Gamma),$$

where K_x is the distribution coefficient (the ratio of the microcomponent concentration in the solid phase to its concentration in the liquid phase); m is the number of ions into which the microcomponent $A_{n_1}B_{n_2}$ dissociates ($m = n_1+n_2$); $b = (K_1 \cdot K_1'^m)/(K_2 \cdot K_2'^m)$ (K_1' and K_2' are the rate constants of adsorption and desorption respectively, of the microelement at the crystal surface; K_1 and K_2 are the rate constants of the "molecules" leaving the surface for the volume of the crystal and of those coming to the surface from within respectively); Z_1 is the amount of microcomponent in a unit volume of the crystal when the concentration of the microcomponent in the solution is infinitely large, whereas the macrocomponent concentration is invariable. Γ is the microcomponent content in one mole of the crystal.

In the region of poor filling

$$K_x^m = b(\alpha' c_o - \Gamma)$$

where α' is a constant and c_o is the microcomponent concentration in the initial solution.

This equation accounts for the appearance of a lower miscibility limit: as the microcomponent concentration goes down so does also the value of the distribution constant, i.e., the mixed crystals become lower in the microcomponent. The absence of a lower miscibility limit is connected with the formation of homogeneous anomalous mixed crystals, which from the thermodynamical standpoint represent a single phase.

The kinetic method was used in computing the distribution of cations between the solid and liquid phases for anomalous mixed crystals when no microcomponent aggregates are formed in the macrocomponent crystal. Equations establishing a relation between the time of recrystallization and the amount of microcomponent in the precipitate were obtained. These equations for true isomorphous systems resemble a simple exponential law of exchange, differing only in pre-exponential factors.

Murin and Pliner (16) also have investigated the formation mechanism for anomalous mixed crystals and have theoretically derived analytical expressions for the activity of the microcomponent in heterogeneous systems. There are grounds to suggest that no anomalous mixed crystals will form unless the number of microcomponent particles in 1 millilitre of solution, C, exceeds a certain critical value, $C_{cr.}$, at which the monolayer on the crystal surface becomes unstable and disintegrates into two stable surface phases. If $C > C_{cr.}$, the monolayer of microcomponent (the "guest") is stable enough to defy its replacement by the macrocomponent (the "host") when the latter is in progress of crystal growth. If $C < C_{cr.}$, no formation of condensed phase will take place.

Also considered is the role in those processes of the association of particles on cocrystallization to form complexes in the broad sense of the word.

Gorstein (17) has published a series of papers on the role of the physico-chemical state of the impurities in the processes of their fractionation on crystallization or when inorganic substances are deposited from aqueous solutions.

New data have been obtained on the distribution of the microcomponent between the melt and the crystal phase. V. R. Klokman and collaborators (18) have found that anomalous mixed crystals do form in the LaF_3-RaF_2 system when lanthanum fluoride is liberated from the KF or RbF melts, yet there is no lower limit of miscibility. The value of the fractionation coefficient depends on the chemical nature of the second component: the value of D is about 2.5 times as great in the RbF melt as in the KF medium. It is of interest to note that enriched by the microcomponent in these experiments was the solid phase and not the melt, as is observed usually. The introduction of microimpurities (Ca^{2+}, Ba^{2+}) had no influence on the value of the fractionation coefficient. Emphasized in this work, as, indeed, in some other investigations, is the important role of complex formation in the melt in the course of fractionation.

Study of the distribution of $PbCl_2$ labelled with ThB between the melt and the LiCl, NaCl, KCl and KBr crystals has shown that the halides of alkali elements having the lattice of NaCl type do not capture lead in appreciable quantities. So there is a striking difference between the behaviour of lead ions in a melt and in aqueous solutions. The authors of the papers cited explain it by a strong dependence of the fractionation coefficient upon the temperature.

Adsorption of radioactive isotopes from solutions has been the object of a number of investigations. Thus I. E. Starik and collaborators (19) have been engaged in the study of some essential problems bearing on the relation of adsorption processes to such factors as the chemical properties of the ions, the nature of the sorbent and the environmental conditions. Heavy elements of the main subgroups in groups I and II of the periodical table are adsorbed on glass and other sorbents of ionite type in the form of positively charged ions, being unable to form colloids even in ultra-small concentrations. Heavy elements in the III - VIII groups form true colloids, starting from pH = 2-7 upwards. The adsorption of these elements is based on their hydrolytic capacity. On the adsorption curve there is always a maximum. The rise of the curve is due to the ionic portion, its decline, to the colloidal portion.

The adsorption of negative ions has been studied on phosphates. The highest adsorptive capacity towards the HPO_4^{2-} ion was displayed by glasses which had the highest dielectric constant and whose surface was the least negatively charged. The presence on the glass surface of foreign multivalent cations increased the sorptive capacity.

Adsorption of radioactive isotopes Zr^{95}, Nb^{95}, Th^{234}, Pa^{233}, Tl^{204}, and Cs^{137} without ion exchange was measured on paraffins and fluoroplast-4 (20). In a nitric acid solution (0.1 - 5 N HNO_3) a notable adsorption of Zr^{95},

Nb^{95}, Th^{234} and Pa^{233} is observed, owing, probably, to the formation in the aqueous phase of neutral complexes corresponding to the general formula $[Me(OH)_x(NO_3)_y]^0$. If NH_4NO_3 and KNO_3 are added, the adsorption diminishes several times, apparently on account of a salting out effect. If the acidity of the solution increases to 12 N, the adsorption of Zr^{95} and Th^{234} decreases, whereas the adsorption of Nb^{95} and Pa^{233} changes insignificantly. The author's explanation of this fact is that Zr^{95} and Th^{234} form a complex with HNO_3. The Cs^{137} and Tl^{204} ions (in monovalent form) are not adsorbed either on parrafin or on fluoroplast-4, because they refuse to form neutral compounds under the investigated conditions.

The regularities displayed by the adsorption of radioisotopes on various precipitates have been investigated by N. E. Brezhneva and collaborators (21). When the secondary adsorption of cations on an iron oxyacetate precipitate was measured quantitatively with allowance for complex formation, and the pH value of the solution as well as the surface area of the precipitate formed were determined, it was found that within a wide range of concentration of the adsorbed cations the adsorption isotherm is described by

$$q = Ae^{1/n},$$

where q is the amount of the substance adsorbed per 1 g of precipitate. The coefficient n is independent of the pH of the solution and is a function of the charge of the adsorbed cation, whereas the coefficient A depends on the pH value, which influences the specific surface area and the formation of an electric double layer at the solid - solution interface.

It has been established that the adsorption isotherm for cations on precipitates of the hydroxide type can be represented in a developed form by the equation

$$q = \frac{E}{E_o} A\ (pH - pH_o)\ c^{1/n}$$

where E/E_o is a quantity proportional to the specific surface area of the precipitate; pH_o is a value of pH at which the adsorption of the particular cation begins.

The sorption of various radioactive isotopes (Cs^{137}, $Sr^{89,90}$, Ce^{144} and Ru^{106}) on aluminium hydroxide precipitates has been investigated by S. A. Voznesensky and collaborators (22). The tests were run at 20° with microconcentrations of the isotopes. Practically there was no sorption of cesium under test conditions; for the other isotopes sorption was a maximum at certain pH values, viz., at 7.0 for Ru, at 7.5 for Ce, at 9.0 for Sr. As the temperature goes up, the adsorption of Ce and Ru grows, whereas the adsorption of Sr remains practically invariable. The authors suppose that the Ru and Ce ions are adsorbed by an ion exchange mechanism, while the sorption of strontium is due to the formation of aluminate.

Considerable work has been done on the chromatography of radioactive elements. General questions concerning the use of ionites in radiochemistry have been dealt with by

B. P. Nikolsky (23). If the salt background (the concentration or activity of the macrocomponent) is constant, the activity coefficient of the microcomponent will be constant too. The coefficient of microcomponent ion distribution between the ionite and the solution (α_1) is independent of the microcomponent concentration:

$$\alpha_1 = \frac{\Gamma_1}{C_1} = K^{z_1}\left(\frac{\Gamma_2}{C_2}\right)^{z_1/z_2} f\ (\gamma) = \text{const}$$

Here C_1 and C_2 are the concentrations of the respective ions; f (γ) is a factor containing the activity coefficients of the ions in the resin and in the solution; Γ_1 and Γ_2 are the amounts of adsorbed ions belonging to the microcomponent and macrocomponent respectively; z_1 and z_2 are the valence of the respective ions; K is the exchange constant.

This equation is generally used in solving various radiochemical problems.

Some theoretical problems connected with the use of the frontal method in the chromatography of ion exchange complex formation for the production of pure preparations of radioactive isotopes have been tackled by K. V. Chmutov and co-workers (24). The authors have analyzed the principal factor controlling zonal motion in a frontal analysis of a mixture of complex ions present in macro- and microconcentrations. By means of the equations they have obtained for adsorption isotherms and for the frontal motion of the second component, the coefficient of microcomponent enrichment and that of purification of the macrocomponent can be calculated.

This method has been tried by experiment on a mixture of ethylenediaminotetraacetate complexes of Ca^{2+} (macrocomponent) and Sr^{2+} (microcomponent). The results are in good agreement with the theory. With regard to the purification of the macrocomponent, the frontal method has been found to be 18 times as efficient as the ion-exchange displacement method.

The influence of temperature on ion-exchange equilibrium has been studied by Matorina and Popov (25). Their theoretical statements are confirmed by an experimental analysis of temperature variations in ion exchange sorption of Ca^{45} and of fragmentary isotopes - Cs^{137}, Sr^{89} and Ce^{144}-Pr^{144}.

An important cycle of research is formed by investigations into the action of radiation on ion-exchange resins. Various types of resins in different media have been investigated. They were acted upon by X-rays, gamma-rays and by high energy electrons. Proskurnin and co-workers (26) have shown that the radiation destruction of ionites is accompanied by increase in their static exchange capacity. This is evidence that the number of ion-exchanging functional groups, especially hydroxyls, increase in the ionite.

Senyavin et al. (27) have investigated three typical ionites for their resistance to X-rays and gamma-rays, viz., $K\mu$-1 (sulphocationite of the phenol-formaldehyde type), $K\mu$-2 (sulphurated copolymer of styrene and divinylbenzene), and KB-4 (saponification product of a copolymer formed by methyl metacrylate and divinylbenzene with carboxyl functional groups). It has been found that the effect of radiation is to induce competing processes of destruction and cross-linking. The chemical alterations caused by radiation are deeper in resins of aliphatic structure than in those with aromatic character. Qualitatively the functional groups of the cationites studied are resistant to radiation, though they decrease somewhat in quantity. The highest resistance was shown by the Kμ-2 cationite.

Kiseleva and Chmutov (28) have subjected the Kμ-2 cationite to bombardment by high energy electrons. As the radiation dose increased from 10^{21} to 10^{24} eV per g of resin the exchange capacity for the functional group HSO_3^- diminished, and new ion-exchange groups with pK = 4.3 and 7 made their appearance. The resin partly passed to a soluble state. By irradiating the Kμ-2 cationite in different solutions (0.5 N HNO_3, 0.5 N CH_3COOH and a 0.25 N solution of ammonium lactate) new functional groups can be made to appear even with a dose of 10^{22} eV per g of resin.

Work in the field of chromatographic separation of radioactive isotopes has been so extensive that only a few instances can be referred to here. Especially strong is the number of investigations concerned with the separation of fission rare earth isotopes. Tunitsky and collaborators (29) have developed a theory of chromatographic separation of rare earth elements in which account is taken of statistical factors (the ratio of sorption coefficients of the separated ions) and of kinetic factors (the rate of diffusion of the ions in the sorbent grains, their rate of diffusion to and from the grains in a flow of solution, longitudinal mixing and diffusion). Experiments have shown that the diffusion coefficients of rare earth elements grow in the order of their atomic numbers. On the suggested theory the optimal conditions for the separation process and its duration can be computed.

The separation of fission rare earth elements by means of lactic acid and pyrophosphoric acid solutions has been studied by Maslova, Nazarov and Chmutov (30). The authors measured the stability constants of lactate complexes of some rare earth elements and were able to show that the use of pyrophosphoric acid for the chromatographic separation of rare earth elements holds promise of success.

Preobrazhensky et al. (31) determined the separation coefficients for all rare earth elements, when ammonium lactate is the complex former, and compared them with the available literary data on the oxyisobutyrate and glycolate of ammonium. The authors found that heavy rare earth elements are separated better with ammonium lactate, while for those of smaller atomic weight ammonium oxyisobutyrate is preferable.

To find out how the processes involved in the chromatographic separation of Y from Ce and of Pm from Nd are influenced by the number of carbon atoms in the chain of some α-oxyacids has been the object of experiments arranged by Spitsyn and Voitekh (32). They made use of the following acids as complex formers: glycolic, lactic, α-oxyisobutyric, α-oxyisovaleric and α-oxyisocaproic. The experiments were run by a static method as well as dynamic. It has been found that the separation coefficient of rare earth elements is higher the stronger the proton bond in the α-oxyacid, i.e., the weaker the acid. Increase in the size of the addend (e.g., in the case of α-oxyisocaproic acid) brings about a weakening of the complex. Therefore α-oxyisobutyric acid is the best eluant.

Lavrukhina and co-workers (33) have suggested the use of trioxyglutaric acid for the separation of fission rare earth elements (La, Ce, Pr, Nd). She has also studied the effect which the quantity of elements has on the shape and position of the peaks on the yield curve in the chromatographic ion-exchange separation of rare earth elements. As the quantity of elements goes down the rate of their elution goes up in a number of cases. This is probably because the equilibrium in the eluant solution is shifted towards the complex form. With ultrasmall concentrations the observed shift of the peaks can unfavourably affect the outcome of the separation process.

For some closely related elements the chromatographic methods of separation have been made more efficient by B. N. Laskorin and collaborators (35). This they achieved by the use of appropriate complex formers, where by diminishing the effective concentration of the ions separated, which in first approximation is tantamount to decrease in the quantity of the separated elements. Difference in the constants of complex formation is prone to increase the separation coefficient. The authors have investigated nine specimens of cationites and 12 complex formers for the separation of radium and barium. Most effective were the following acids: citric, nitrilotriacetic and ethylenediaminetetraacetic. The rate of production for barium was 50 kg/hour per 1 m^2 of column cross-section.

Spitsyn and Kuzina (36) liberated a few milligrams of technetium from impurities by a chromatographic technique. Spitsyn and D'yachkova (37) evolved a chromatographic method for the separation of protactinium, zirconium, titanium and niobium in a column with manganese dioxide. The sorption of Pa and Nb from 10 N HNO_3 permits Zr and Ti to be separated. Conditions for the separate elution of Pb and Nb from the column were chosen after studying the coefficients of their distribution between MnO_2 and the NH_4F solutions. By this method ponderable quantities of radiochemically pure Pa^{231} were obtained.

Inorganic ionites are of great interest on account of their resistance to radiation. Kraus (38) is known to use zirconyl phosphate for this purpose. In the Soviet Union zirconium based ionites have been investigated by Bresler and co-workers (39), viz., the sulphide, chromate, arsenate, oxalate and carbonate of zirconyl. The investigations have shown that all of these compounds have ion exchange properties. When taken in the H^+ form, they secure a good separation of related elements, e.g., Ca^{2+}-Mg^{2+}, Sr^{2+}-Ca^{2+}, and others. As the eluting solution, 0.05-0.5 N HCl was employed. The enrichment obtained for the microcomponent ranged from 0.5×10^2 to 10^4.

Soviet radiochemists have been paying considerable attention to problems connected with the separation of radioactive elements by extraction. As is well known, extraction techniques have found world-wide application in the radiochemical industry for the separation of uranium, plutonium and fission elements, as well as for the production of pure uranium compounds. Experience accumulated in this field was extended to other radioelements, where it contributed to considerable progress. And though applied radiochemistry is beyond the scope of this review it seems appropriate to dwell briefly on the work done in the USSR in connection with the main extraction techniques.

Vdovenko and collaborators (40) have investigated the solubility of various hydrates of uranyl nitrate in diethyl ether and used the methods of physico-chemical analysis for determining the composition of the compounds formed containing water and bound solvent. A systematic study has also been carried out of the uranyl nitrate distribution between aqueous solution and diethyl ether.

Vdovenko and Smirnova (41) have measured the distribution of uranyl nitrate between aqueous solutions and various ethers and esters. The highest equilibrium constants of the processes taking place here were found with diisoamyl ether, chlorex, isoamylbenzoate and dibutyl ether. Moreover the authors investigated the composition uranyl nitrate hydrates formed by extraction of aqueous solutions with diethyl ether and dibutyl ether in the presence of salting out agents (KNO_3, $NaNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$). In diethyl ether the salts capable of binding water decrease the hydration of uranyl nitrate. This does not occur in dibutyl ether, apparently because the hydration of uranyl nitrate in this solvent is slight. Addition of diluents (C_6H_6, CCl_4, $CHCl_3$) brings about a decrease in the hydration of uranyl nitrate and the extracting power of the solvent is reduced too.

Problems connected with the structure of the coordination sphere of uranium in various organic solvents have been discussed by Vdovenko et al. (42).

Shevchenko and co-workers (43) have investigated the use of tributyl phosphate (TBP) as a solvent. They measured the polarization and dielectric constant of TBP mixtures with various diluents and came to suggest that the distribution coefficients of uranyl nitrate are definitely connected with the polar properties of the TBP-solvent system.

Investigation of the influence of TBP hydrolysis products on the extraction of plutonium has shown that in practice this process is not affected if the admixture of monobutyl phosphate is below 0.001 mol/l or that of dibutyl phosphate is below 0.0001 mol/l. Yet with higher quantities of these substances the distribution coefficient of plutonium rises considerably, owing presumably (44) to complex formation in the aqueous phase.

Rosen and Moiseenko (45) have investigated the influence which the concentration of HNO_3 and uranyl nitrate exert on the distribution of Pu (IV) and Pu (VI) in the case of extraction with a 20% solution of TBP in hydrogenated kerosene. In the absence of uranium the increase of HNO_3 concentration leads first to increase and then to decrease of the Pu distribution coefficients. The dependence of plutonium distribution coefficients upon the acidity in the presence of uranium was found to be different for Pu (IV) and Pu (VI). The observed relations can be accounted for by the fact that the salting out effect of macronitrates in the aqueous phase is combined with the displacing effect in the organic phase.

Experiments with the extraction of uranium by TBP from hydrochloric acid solutions have shown that the compound $UO_2Cl_2 \cdot 2TBP$ is formed in the organic phase (46,47).

A large number of different solvents have been tried for the extraction of uranium, plutonium and other radioactive elements.

Laskorin, Zefirov and Skorovarov (48) have investigated some dozens of organic solvents which seemed well fitted for the extraction of uranium from solutions and ore pulps. Among them were esters of carboxylic acids, phosphoric ester, phosphinic ester as well as liquid cationites and anionites. Some of these substances were used with diluents. Most promising for uranium extraction from nitrate media are isoamyl acetate, dimethyl phthalate, dibutyl ether and a 5-10% solution of TBP in kerosene.

For uranium the diisoamyl ether of methylphosphinic acid proved to be effective as a solvent. With it the distribution coefficients are higher than with TBP. The composition of the complexes which this extracting agent forms with uranyl nitrate and HNO_3 has been determined (49).

A systematic investigation of the complex formation by uranyl nitrate with various organo-phosphorus compounds has been carried out by M. F. Pushlenkov et al. (50). The authors have found the phosphoryl group to play an important part in the formation of uranium complexes: the complex formation constants increase in the series of addends $(C_4H_9O)_3PO \longrightarrow (C_4H_9)_3PO$. The stability constants of complex compounds formed by uranyl with TBP, di-n-butyl ether, n-butyl-phosphinic acid and tri-n-butyl-phosphine oxide have been determined.

It has been shown that an acetate compound of uranium can be extracted with aniline (51). Thereby a triacetate complex is formed with aniline in the external sphere: $C_6H_5NH_3[UO_2(CH_3COO)_3]$.

The application of the extraction technique to processes of separation and purification of various radioelements has been tried by many workers.

Shevchenko and collaborators (52) have described the extraction of protactinium with alkylphosphoric acids. The experiments were run with Pa^{233} in nitrate solutions. The highest distribution coefficients were displayed by dibutyl phosphate, diisobutyl phosphate and diisoamyl phosphate. Used as diluents were isoamyl acetate, dibutyl ether, hydrogenated kerosene and some other products which did not affect the extraction yield. The protactinium distribution coefficients varied proportional to the square of the extracting agent concentration in the organic phase.

The extraction of protactinium with mono- and diisoamylphosphoric acid has been studied by those authors in greater detail. They suggest that the extracting agent here forms complexes in the aqueous phase. Going over into the organic phase is, apparently, the compound PaK_5 (K being the radical of isoamyl phosphoric acid), while the products of its partial hydrolysis $[Pa(OH)_3K_3]^-$, $[Pa(OH)_4K_2]^-$ and others, are in the aqueous phase.

The extraction of pentavalent neptunium has been described by Alimarin and co-workers (53). The tests were run with tracer quantities of Np^{239} and ponderable quantities of Np^{237}. A solution of 1-nitroso-2-naphthol in n-butyl alcohol and in isoamyl alcohol with pH 9-10 was the extracting agent. Up to pH 6 no extraction of neptunium will occur. Forming in the extraction process seems to be a compound of the NpO_2^+ ion with 1-nitroso-2-naphthol. This technique can be used for the separation of neptunium from plutonium and uranium (for their extraction in the presence of 1-nitroso-2 naphthol the solutions should be adjusted at pH 1.0-1.5 and 3.5-4.0 respectively).

Extraction with methylethyl ketone was used for the separation of technetium from irradiated molybdenum (54). For salting out KOH, K_2CO_3 and $(NH_4)_2CO_3$ were employed. Molibdate solutions too are endowed with salting out effect. The re-extraction of technetium from the organic phase was done with a 6 N solution of K_2CO_3.

Diamylphosphoric acid was used by Brezhneva and co-workers (55) for the separation of rare earth fission elements by extraction. The study of this process has revealed that in the region of low hydrogen ion concentrations an organic salt of rare earth elements is the compound extracted. With high hydrogen ion concentrations the extraction mechanism is different: extracted here are $Me(NO_3)_3 \cdot H_2A_2$ solvates (H_2A_2 standing for diamylphosphoric acid), formed under participation of the oxygen of the phosphoryl group.

The effect of uranyl nitrate on the distribution of Cs, Ca, Sr and La between the aqueous solution and methylbutylketone has been investigated by Vdovenko et al. (56). The distribution coefficients of these elements increase as the concentration of uranyl nitrate rises, which fact is ascribed by the authors to the formation of $MeUO_2(NO_3)_2$ compounds in the organic phase.

Considerable work has been done on the chemistry of individual radioelements. Special attention was given to the study of plutonium and the nearest transplutonium elements.

Some unknown or scarcely studied plutonium compounds were synthesized and their properties described. By evaporating a hydrochloric acid solution of hexavalent plutonium in vacuo a crystalline plutonyl chloride, $PuO_2Cl_2 \cdot 6H_2O$ was obtained (57). Plutonyl fluoride, PuO_2F_2, was produced by the action of liquid hydrogen fluoride on a cooled plutonyl chloride solution. The solubility of this compound in water (1.07 g/l at 20°C), its absorption spectra and crystal structure were determined (58). V. V. Fomin et al. (59) has synthesized plutonium tribromide by the action of gaseous HBr at 500°C upon plutonium oxalate (IV).

The properties of nitric acid solutions of hexavalent plutonium have been investigated (60). The hydrolysis reaction constants of plutonyl ion have been computed, and the hydrate of plutonyl nitrate, $PuO_2(NO_3)_2.6H_2O$ has been obtained in the pure form. The radiolytic reduction of Pu (VI) in nitrate solutions under the action of its own radiation was also investigated. It was found to proceed at the expense of atomic hydrogen formed on the radiolysis of water. Pu (VI) is reduced in the form of hydroxy compounds, e.g., PuO_2OH^+. First Pu (V) is formed and afterwards Pu (IV), which disproportionates to Pu (VI) and Pu (III).

The conditions of disproportionation of Pu (IV) and

Pu (V) in HNO_3 solutions have been studied in detail (61). At the start of the process the disproportionation of Pu (V) proceeds as follows: Pu (V) + Pu (V) $\rightleftarrows$ Pu (VI) + Pu (IV). Later on, with the accumulation of Pu (III), the reaction Pu (V) + Pu (III) $\rightleftarrows$ 2 Pu (IV) becomes predominant, which brings about an autocatalytic acceleration of the process.

Also investigated was the solubility of some scarcely studied plutonium compounds, e.g., plutonyl oxalate, $PuO_2C_2O_4.3H_2O$ (62), the bisubstituted phosphate of plutonium (IV) (63) and others.

The salicylates of tri- and tetravalent plutonium have been described by Zviagintsev and Sudarikov (64).

There have been considerable developments in the chemistry of complex compounds of transuranium elements.

Gel'man and her co-workers have investigated the carbonate, oxalate and ethylenediaminetetraacetate complexes of plutonium. In paper (65) is described the production of the carbonate complexes of plutonium (IV): $(NH_4)_4[Pu(CO_3)_4].H_2O$, $(NH_4)_6[Pu(CO_3)_5].nH_2O$ and $(NH_4)_8[Pu(CO_3)_6].nH_2O$. On their decomposition plutonium (IV) oxycarbonate, $PuOCO_3.2H_2O$, is formed. A complex carbonate of plutonium (VI), $(NH_4)_4[PuO_2(CO_3)_3]$, has been isolated by Drabkina (66). It decomposes to form a monocarbonate, PuO_2CO_3.

Solubility measurements were used by Moskvin and Gel'man (67) for determining the composition and instability constants of complex oxalate ions $[Pu(C_2O_4)]^{2+}$, $[Pu(C_2O_4)_2]^{\circ}$,

$[Pu(C_2O_4)_3]^{2-}$ and $[Pu(C_2O_4)_4]^{3-}$. They have shown that among the different valence states of plutonium the tendency to complex formation declines in the order $Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^{+}$. Mixed carbonate-oxalate complexes of plutonium (IV) are described in (68).

In a pure state some oxalate complexes of plutonium (IV) were obtained by Gel'man and Sokhina (69). Unlike the normal oxalate, they are easily soluble. Isolated were the following complexes: $Na_4[Pu(C_2O_4)_4].5H_2O$, $K_4[Pu(C_2O_4)_4].4H_2O$, $K_6[Pu(C_2O_4)_5].4H_2O$, $(NH_4)_6[Pu(C_2O_4)_5].nH_2O$. They proved stable in aqueous solutions both in the cold and when heated. It is interesting to note that one of these complexes, viz., $(K, Na)_4[Pu(C_2O_4)].4H_2O$ can exist in two crystal modifications - red and greenish yellow.

Gel'man and her co-workers (70) used the ion exchange technique in studying the possibility of a complex formation of pentavalent plutonium with ethylenediaminetetraacetic acid (EDTA). Indeed they have established the presence of a complex ion $[PuO_2Y]^{3-}$, (Y^{4-} being the anion of EDTA) in the pH 4-5 region. Measurements of the constant of concentration instability of this ion have shown that it is close to the value reported in (71) for a similar complex of neptunium. For trivalent plutonium with EDTA, complexes of the composition PuY^- and $PuHY^o$ have been found and their structures discussed (72).

Kondratov and Gel'man (72) have investigated oxalate complexes of tetravalent plutonium by means of solubility measurements. The salt $(NH_4)_4[Pu(C_2O_4)].nH_2O$ was isolated by them in the crystalline state. The concentration instability constants of the complexes $[Np(C_2O_4)]^{2+}$, $[Np(C_2O_4)_2]^{o}$, $[Np(C_2O_4)_3]^{2-}$, $[Np(C_2O_4)_4]^{4-}$ were computed. They were found to have the same order of magnitude as the respective Pu (IV) complexes.

New data have been obtained on the chemistry of americium (74). The content of Am (III), Am (V) and Am (VI) in solutions prepared by interaction between AmO_2 and H_2SO_4 has been determined spectrophotometrically. The results show the existence of two reactions:

$$2\ Am^{4+} + 2\ H_2O \ = \ Am^{3+} + AmO_2{}^{+} + 4\ H^{+} \quad \text{and}$$
$$Am^{4+} + AmO_2{}^{+} \ = \ Am^{3+} + AmO_2{}^{2+}$$

Both of them proceed at a high rate, which accounts for the absence of Am (IV) in aqueous solutions.

Moskvin, Khalturin and Gel'man (75) used an ion exchange technique in studying the formation of complexes of Am (III) with EDTA and with oxalic acid. The structure of the compounds which are formed here, viz., $[Am(C_2O_4)_2]^{-}$, $[Am(HC_2O_4)_3]^{o}$ and $[Am(HC_2O_4)_4]^{-}$, is discussed in their paper.

Progress can also be recorded in the chemistry of fission elements. The object of N. E. Brezhneva and her co-workers (76) was to study in detail how the radioisotopes of zirconium, niobium, ruthenium, strontium, barium and the rare earth elements are distributed between the precipitate (calcium oxalate, calcium nitrate, iron hydroxide, etc.)

and the solution. Developed in these studies was an elaborate scheme for the separation of fission elements. It is based on reactions involving co-precipitation. Thus strontium and rare earth elements are deposited with calcium oxalate precipitates; zirconium, niobium and ruthenium, with iron hydroxide. The later group of the elements are separated by liquid extraction with tributyl phosphate from nitrate solutions. On this scheme strontium-90, zirconium-95, niobium-95, ruthenium-106, prometheum-147, cerium-144 and europium-155 can be obtained at the laboratory as pure isotopes in quantities varying from 15 millicuries to 15 curies according to their content in the initial solution.

Other radioelements too have been investigated to some extent by Soviet workers. B. P. Nikolsky and collaborators (77) have used an ion exchange technique in studying the formation of complexes by radium and barium in solutions of EDTA and nitrylotriacetic acid. At pH 5.5-6.9 radium forms with EDTA a complex of the composition $(RaA)^{2-}$. With nitrylotriacetic acid the complex has the composition $(RaX)^{-}$ and is obtained at pH 6-8. The two complex ions are somewhat less stable than the respective barium compounds.

Ziv and Efros (78) measured the solubility of polonium (IV) hydroxide by a microchemical technique, and found it to be $(3.7 \pm 1.5).10^{-5}$ mol/l for pH 6.

Capture of protactinium-233 by various precipitates was studied by Nikolaev and collaborators (79). They have found that Pa is precipitated together with almost every poorly soluble compound of Th. However, when thorium fluoride is precipitated, Pa can be held in solution under certain conditions. The authors suggested the method of "similar carriers" ($CaCO_3$ and $CaC_2O_4.H_2O$) which permits Pa to be separated quantitatively from the oxycarbonate and oxalate of Th, and transferred to other carriers, such as $Fe(OH)_3$. A technique for the extraction of Pa with acetone in the presence of salicylic acid has been developed.

Starik and Sheidina (80) proposed a convenient procedure for radiochemical purification of protactinium by its precipitation together with zirconium phenyl glycollate.

Spitsyn and Kuzina (81) have designed a technique for the isolation of technetium from neutron irradiated molybdenum, and investigated the chemical properties of some technetium compounds.

A great many investigations in the Soviet Union have been devoted to the chemistry of uranium and its complex compounds. However, the results obtained in this field cannot be reported here on account of the space available.

Considerations of space preclude also a discussion of research connected with the production of radioactive isotopes without carriers, although significant progress has been made in this field too.

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THE DEVELOPMENT OF RADIATION CHEMISTRY IN THE U.S.S.R.

by

V. I. Spitsyn and A. K. Pikaev

Contents

1. Introduction

The study of chemical changes of substances brought about by high energy radiation has begun its rapid development in connection with the availability of the large ionizing radiation sources. The development of radiation chemistry was stimulated first of all by requirements of nuclear engineering and problems of the reliable protection against the hazardous radiation.
On the other hand, radiation chemistry deals with the phenomena accompanying high-excitation and high reactivity particles, i.e., ions, free radicals, and molecules. The latter is caused by the fact that energy of ionizing radiation is many times as large as the chemical bond energy. The generation of excited

particles mentioned is the main distinctive feature of radiation-chemical processes in comparison with the photochemical where such phenomena do not almost occur. This circumstance has also promoted the growth of interest in radiation chemistry and its uses in practice.

Russian and soviet scientists have made a substantial contribution in the development of radiation chemistry. Thus, among the first investigators having observed chemical effects of ionizing radiation upon diverse compounds there was N. A. Orlov. In 1904-1906 he found (1) that paraffin, wax, stearic acid and other solid organic substances could be converted into liquid resinous products. In 1910 N. D. Zelinsky (2) placed in a sealed tube some little crystals of radium bromide containing 0.5 mg of pure radium and 1.5 ml of cyclohexene (C_6H_{10}). The investigation carried out after several years revealed the deposition of free carbon on surface of the bromide crystals, the liquid decomposition products consisting not only of hydrocarbons more simple than cyclohexene but, also, of more heavy hydrocarbons synthesized under action of alpha particles emitted by radium. As an intermediate process, apparently, dehydrogenation of the original material occurred.

N. D. Zelinsky stated that relative processes could take place in nature under effects of radiation of radium contained in rocks.

Modern development of radiation chemistry in this country has begun in the post-war years, being caused by uses of nuclear power for various purposes. This period is characterized by rapid development of wide-scale research work embracing more and more diverse classes of compounds and reaction types and, on the other hand, by employment of modern research techniques involving gas-liquid chromatography, electron paramagnetic resonance, mass spectrometry and so on for identification of radiolysis products and for elucidation of the reaction mechanism. As ionizing radiation sources, nuclear reactors, spent fuel elements of atomic power reactors, γ-ray sources of Co^{60} and Cs^{137}, α-emitters such as radon and polonium preparates, betatrons (including these with extracted electron beams), electron accelerators permitting both continuous and pulsed irradiation, X-ray installations, and so on are employed.

There are radiation-chemical research laboratories in various regions of the USSR. A number of the Moscow research institutes are carrying out investigations in this field. Radiation-chemical investigations are accomplished in the Ukrainian SSR, Georgian SSR, Uzbeck SSR and other republics having atomic reactors. The fact that in the last three years about three hundred publications on this topic have been issued by soviet investigators illustrates the development of radiation chemistry in this country. In 1957 the first All-Union conference on radiation chemistry was held in Moscow, where 56 papers were reported and discussed (3). A large number of the soviet investigations in this field have also been reported in other scientific congresses and conferences in this country as well as abroad (4-10).

The authors of this paper shall, in the main, describe the most important directions of research in radiation chemistry in the USSR and also shall review some interesting papers published in 1958-1960. The previous soviet works are published in the form of separate collections (11-12), transactions of a number of conferences (4-7), and are also told in reviews (13-16) and booklets (17-18) edited in the USSR.

2. Radiation chemistry of water and aqueous solutions

The radiation-chemical reactions occurring in water and aqueous solutions were an object of many investigations carried out during the last years in this country. This is caused first of all by the fact that water is used as a moderator and a coolant in atomic reactors; besides, in aqueous solutions many processes take place involved in the nuclear fuel production and isolation of nuclear reaction products. Moreover, behaviour of aqueous solutions under irradiation is analogous, in a considerable extent, to that of biological systems. That is why the study of the effects of ionizing radiation up on the aqueous solutions can be assumed as basis for estimation of the effects of radiation on living tissue.

Soviet research works cover a wide range of diverse questions of the radiation chemistry of water and aqueous solutions. The influence of an ionization density and dose rate on the yields of radiolytic conversion in the aqueous solutions, the role of direct action of radiation on dissolved substance, the role of excited molecules of water in radiolysis processes, and the dependence of the yields of molecular products of radiolysis on concentration of solution were ascertained. Radiation-electrochemical processes and the influence of irradiation on corrosion behaviour of metals and some other questions were an object of a number of investigations.

At present it is generally accepted that under the action of radiation on water atoms H and radical OH, as well as molecular hydrogen and hydrogen peroxide, are generated as primary products of the radiolysis. These intermediate products interact further with the dissolved compound. In the case of the diluted aqueous solutions it is possible in this way to explain the character and the yield of the radiolysis products and, in some cases, the radiolysis kinetics also. Based on this conception systematic investigations are carried out in the USSR. V. Yu. Filinovsky and Yu. A. Chizmadzhev (19) have made calculations concerning the dependence of the molecular products yield in the case of the radiolysis of water under the action of radiations with high ionization densities in the presence of scavengers. Two cases of atoms H and radicals OH distribution during water radiolysis have been considered: 1) both radicals are in a track column with the diameter ≈1 Å and 2) atoms H have more diffusive distribution (≈100 Å).

B. V. Ershler et al. (20) have compared the rate of radiation-chemical decomposition of hydrogen peroxide with the most reliable data available in the world literature concerning the radiolysis of water under the action of γ-radiation of cobalt-60.

The authors have confirmed the applicability of the hypothesis about the constancy of yields of radiolysis products of water as well as the adequacy of the law of homogeneous kinetics to the case of radiation chemical processes in diluted aqueous solutions.

In another paper B. V. Ershler (21) basing on the model of irradiated solution in which free radicals and molecular products are distributed homogeneously in the total irradiated volume, has considered general regularities of the radiolysis, for the cases wherein this model is applicable. Proceeding from the assumption that radiolysis products yields of water are constant values and that in the solution only bimolecular reactions proceed, the author has considered the effects of radiation intensity on the dependence of yield upon concentration. Two criteria for the adequacy of this model have been found. In the case of stationary state, the increase of intensity from I_1 to I_2 displaces the curve representing the dependence of a logarithm of concentration of one of radiolysis product upon a logarithm of concentration of another product, along the coordinate axes by a segment which is equal to $\Delta I^{1/2}$, the shape of the curve being unchanged. If stationary state is not yet achieved, the variation of intensity leads to displacement by the same value $\Delta I^{1/2}$ along the abscissa of the curve representing the dependence of the radiation yield G of one product with logarithm of concentration of another. Radiolysis of the solutions of hydrogen peroxide (20) is an example of such a regularity.

It is known that increase of concentration can bring the conditions in which the dissolved compound would interact not only with free radicals distributed in whole volume of solution but also with those in the points of high ionization density, competing thus with the recombination reaction of radicals and reducing the molecular product yield. In this connection the investigations of P. I. Dolin with collabor., N. A. Bakh with collabor., and M. A. Proskurnin with collabor., are of considerable interest. Examining the nitrate systems (22-24), as well as the aqueous solutions of potassium bromide (25-26), it has been found that a substantial part of molecular hydrogen originates from the recombination of atoms H. For instance, decreasing of magnitude of G (H_2) till some hundredths of molecules per 100 electron-volt with the increasing NO_3^--ions concentration has been found (22-24).

Of considerable interest from the point of view of elucidating the mechanism of radiolysis oxidation of Fe^{++}-ions in diluted aqueous solutions is the work of V. N. Shubin and P. I. Dolin (27), in which the effects of pressure of hydrogen above the solution on the yield G (Fe^{+++}) is investigated. It was found that variation of the pressure of hydrogen in the range from 1 to 180 atm. does not exert an appreciable influence on the system concerned. A mechanism has been suggested for this case which includes the following reactions:

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-$$

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH + OH^-$$

$$H_2 + OH \longrightarrow H_2O + H$$

$$H + H^+ \longrightarrow H_2^+$$
$$Fe^{++} + H_2^+ \longrightarrow Fe^{+++} + H_2$$

The results obtained confirm the hypothesis according to which in deaerated solutions H atoms take part in oxidation of Fe^{++}-ions, directly or by means of formation of H_2^+-ions.

It is known the yields of radical and molecular products of water radiolysis are dependent on the magnitude of linear energy transfer, i.e., on the kind of radiation. Although a number of soviet investigations hitherto carried out in this topic is not large, they are of definite interest. A. M. Kabakchi et al. (28-29) investigated effects of γ-radiation of cobalt-60, β-rays of phosphorus-32 and α-particles of plutonium-2 on aqueous solutions of nitrates in various concentrations. Radiation-chemical yield of NO_2^-, according to the authors mentioned is dependent on the kind of the radiation. For instance, under the action of α-radiation of Pu^{239} $G(NO_2^-)$ is considerably less, than that in the cases of γ-rays of Co^{60} and β-particles of P^{32}.

Z. V. Ershova and M. V. Vladimirova (30) have studied the action of alpha-particles of polonium on 0.8 N aqueous solutions of H_2SO_4. It has been found that the initial yield of hydrogen peroxide (1.2 molecules per 100 ev) is independent of the concentration of polonium dissolved in the range of specific activity from 0.1 to 12 millicure per ml, concentration of H_2O_2 tending to its limit value. For 0.8 N H_2SO_4 the equilibrium limiting value of the H_2O_2 concentration amounts to $5\text{-}8.10^{18}$ molecules per ml.

S. A. Brusentseva and P. I. Dolin (31) have investigated the action of 660 Mev protons on aqueous KBr solutions. The linear energy transfer of the radiation mentioned is nearly to that of 1 Mev electrons. The work has demonstrated that the radiation-chemical phenomena are defined solely by the magnitude of the linear energy transfer. Thus the yields $G(Fe^{+++})$ obtained in the case of aqueous ferrous sulphate solution and $G(H_2)$ obtained for KBr solutions of various concentrations (Fig. 1) have been found by the mentioned authors to be approximately equal to the corresponding values obtained under action of γ-radiation of Co^{60}.

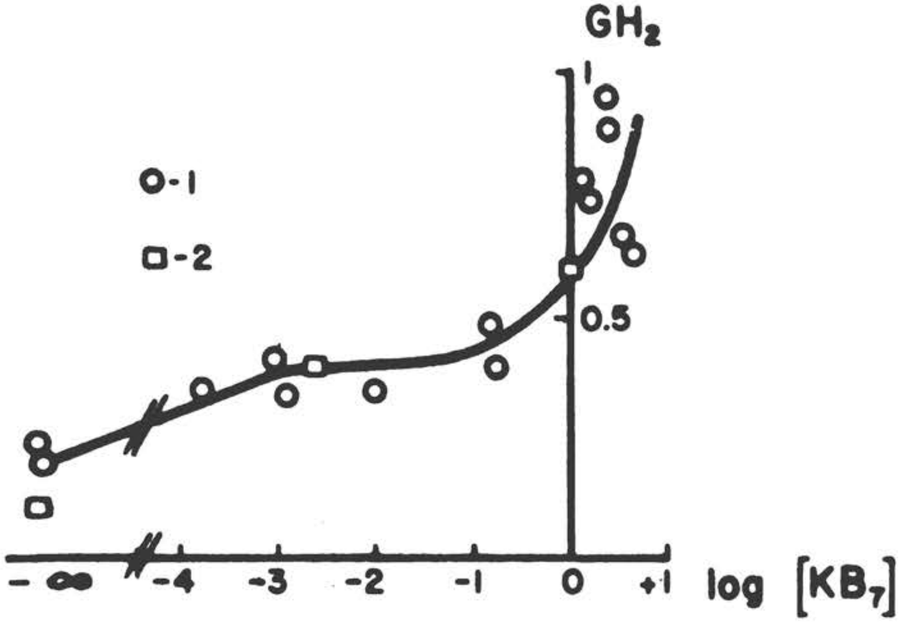


Fig. 1. The dependence of $G(H_2)$ on molar concentration of KBr solution under the action of protons with energy 660 Mev (1) and γ-radiation of Co^{60} (2).

A. K. Pikaev and P. Ya. Glazunov (32-37) have studied radiolytic transformations in aqueous solutions of several inorganic compounds at high dose rates. The latter have been achieved by means of pulsed electron radiation; the electron energy has been 0.8 - 1.0 Mev; the pulse duration - 5 μsec. The radiolytic conversions in aqueous solutions of ferrous sulphate and ceric sulphate, of the mixtures of Ce^{++++} and Tl^{+} sulphates and also Ce^{++++} and Ce^{+++} sulphates have been investigated. Fig. 2 indicates the dependence of G (Fe^{+++}), G (Ce^{+++}) in the absence of Tl^{+}, and also G (Ce^{+++}) in the presence of Tl^{+} upon dose rate, obtained by the authors. As one can see from Fig. 2, appreciable variation of yields takes place at the high dose rates up from about 10^{21} ev/ml sec. For instance, G (Fe^{+++}) decreases with increase of the dose rate, whereas G (Ce^{+++}) under the same conditions increases. This is caused by the fact that at the dose rates up from $\sim 10^{21}$ ev/ml.sec and higher the processes originated by overlapping of ionizing particle tracks begin to play a significant part, changing the yields of radiolysis products of water G (H), G (OH), G (H_2) and G (H_2O_2).

In the papers mentioned above (32-37) it has also been observed that at high dose rates the importance of competition between radical-radical and radical-solute reactions is augmented. Fig. 3 shows the dependence of the yields of radiolytic conversion in several systems upon the concentration of dissolved substance at high dose rates of radiation, found in above mentioned works.

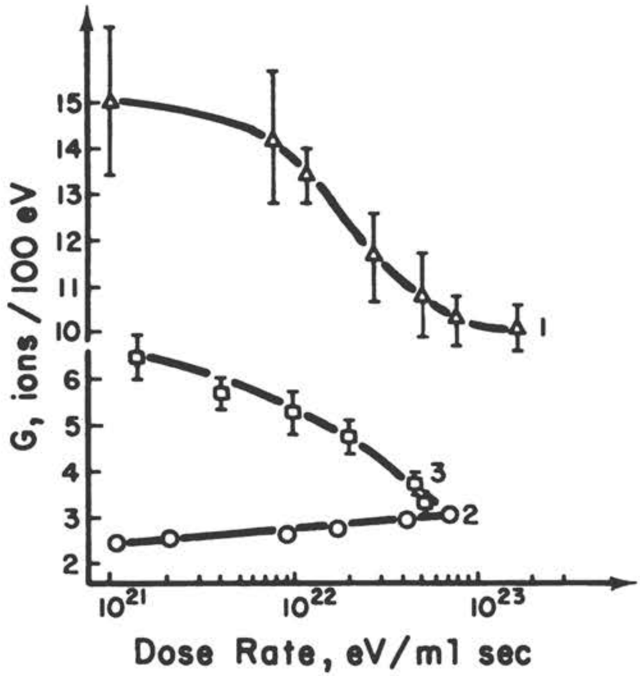


Fig. 2. The effect of high dose rates of radiation upon the yields of radiolytic transformations in aqueous 0.8 N sulfuric acid solutions, saturated with air:

1 - the dependence of $G(Fe^{+++})$ on dose rate in 3.10^{-3}M solution of ferrous ammonium sulfate;

2 - the dependence of $G(Ce^{+++})$ on dose rate in 2.10^{-4}M solution of ceric sulfate;

3 - the dependence of $G(Ce^{+++})$ on dose rate in solution of the mixture of $Ce(SO_4)_2$ and $Tl_2\ SO_4$ (concentration is 2.10^{-4} and 1.10^{-2} respectively)

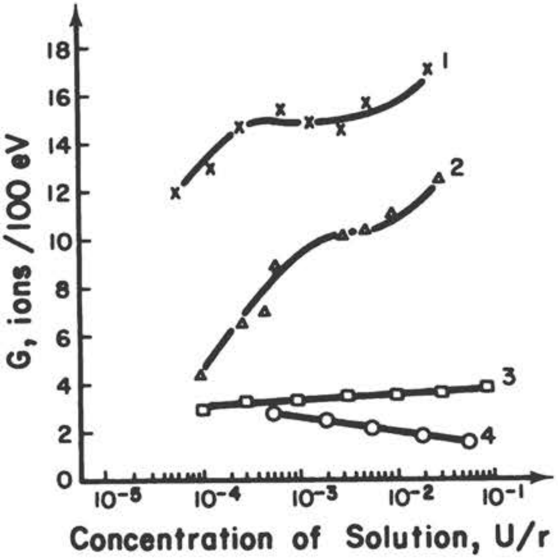


Fig. 3. The dependence of the yields of radiolytic transformations on concentration of solution at high dose rates of radiation

1 - the effect of concentration of ferrous ammonium sulfate in aqueous 0.8 N sulfuric acid solution saturated with air on G(Fe^{+++}) at dose rate 10^{21} eV/ml. sec;

2 - the same at dose rate $3,5.10^{22}$ eV/ml. sec;

3 - the effect of concentration of thallous sulfate in 0.8 N sulfuric acid solutions of the mixture of Ce^{++++} and Tl^{+} salts saturated with air on G(Ce^{+++}) at dose rate $4,5.10^{22}$ eV/ml. sec;

4 - the effect of concentration of cerous sulfate in 0.8 N sulfuric acid solution of the mixture of Ce^{++++} and Ce^{+++} salts on G(Ce^{+++}) at dose rate about 5.10^{22} eV/ml. sec.

The mechanism of radiolytic transformations in concentrated solutions is a problem today. In this case not only the effects of radiation caused by the action of water radiolysis products on the dissolved substance take place, but also direct action of radiation on it is involved. A. M. Kabakchi is one of the first investigators having proposed the conception of direct action (38). He has shown that in the radiolysis of aqueous chloride solution molecular chlorine is formed, the yield of which increases in proportion to increasing solute concentration independently of the kind of radiation or the cation nature.

A different point of view has been suggested by M. A. Proskurnin et al. (14, 23-24, 39-43). According to their hypothesis the high concentration gives possibility to radicals originated not only from ionized molecules of water, but also from excited molecules to be involved in the radiation-chemical reactions. In Fig. 4 the dependence found by the authors mentioned above (24) is shown, between the yield G (NO_2^-) and concentration of $NaNO_3$ solution. The radiation yield G (NO_2^-) increases with augmentation of $NaNO_3$ concentration reaching a constant value in the region 5.10^{-4}-10^{-2} M. The authors have suggested that existence of this slightly sloping segment of the curve can be explained by involving of practically all the H-atoms formed in the reaction with nitrate-ions. In the more concentrated solutions the yield G (NO_2^-) increases again, and for the 1-6 M solutions remains constant. According to the authors (24) the increase of the yield G (NO_2^-) in the concentrated solutions is caused by involvement in the process of the H-atoms originated from both the ionized and excited molecules of water.

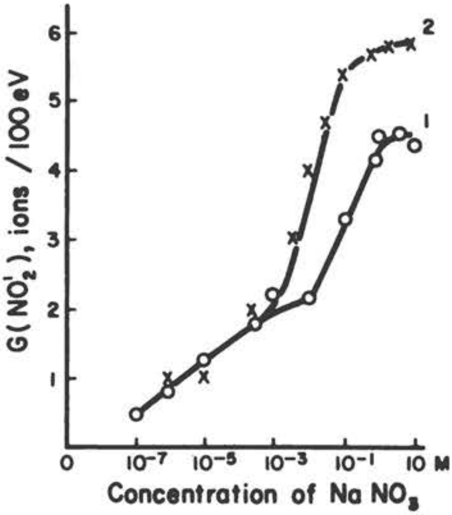


Fig. 4. The dependence of $G(NO_2^-)$ on concentration of $NaNO_3$ in solution saturated with nitrogene (pH=14):
1 - in absence of glycerol
2 - in presence of glycerol at 10^{-3} M concentration.

It is M. A. Proskurnin who has discovered the radiation sensibilization phenomena described below. If in a solution one adds a substance capable of interacting easily with one of the radical radiolysis products of water, there are created conditions in which other radicals are more completely involved in radiolytic conversion. In the case of nitrate systems according to (14, 39, 44) such substances are glycerol and glucose. Being active acceptors of OH-radicals these promote G (NO_2^-) to be higher.

Curve 2 in Fig. 4 represents the dependence of G (NO_2^-) on concentration of $NaNO_3$ solution in the presence of glycerol. Here the yield G (NO_2^-) in the case of highly concentrated solutions reaches a value of ~6 ions/100 ev, what implies involving of all water radiolysis products in the reaction with dissolved substance.

Recently, M. A. Proskurnin et al. (45) have proposed the hypothesis according to which there are two kinds of excited molecules of water differing in level and type of excitation. This hypothesis can explain the existence of three limiting values of the radiolysis yield of dissolved substance in dependence on various conditions of radiolysis. In the case of the nitrate system, as was mentioned above, the limiting values of G (NO_2^-) are equal to 2, 4, and 6 ions/100 ev.

Radiolytic transformations in concentrated aqueous solution have been investigated by a number of other soviet scientists. The work of L. T. Bugaenko and V. N. Belevsky (46) dedicated to the problem of direct action of radiation on the concentrated perchloric acid aqueous solutions is of a certain interest.

As it has been found by A. A. Balandin, V. I. Spitsyn et al. (47), under the effects of irradiation on aqueous solutions of several complex salts of platinum the precipitation of metallic platinum takes place, the product having a higher catalytic ability in the low-temperature reaction of cyclohexene hydrogenation. Palladium black prepared on by the radiation-chemical method differs, according to the same authors (48), by its catalytic properties from the material prepared in conventional way.

Radiolytic transformations in aqueous solutions of plutonium have been examined by H. A. Bakh and collab. (49, 50). Several papers of soviet authors are devoted to radiolysis of aqueous solutions of uranium (51, 52). V. G. Firsov and B. V. Ershler (51) examining radiation-chemical reactions in aqueous solutions of uranium (IV) have found that under the action of γ-radiation of Co^{60} radicals OH and hydrogen peroxide are responsible for oxidation of U^{+4}-ions. As concentration rises, the oxidation yield at first increases and subsequently is lowered. In the presence of oxygen G (UO_2^{++}) is significantly more (16 eq/100 ev) than that in the degassed solutions. The authors have deduced the equation describing the dependence of G (UO_2^{++}) upon U^{++++} concentration, the ratio of the rate constants of the three reactions (U^{+4} + OH, H + OH and H + H) being involved.

G. N. Yakovlev with collab. (53) examining the effects of inherent α-radiation of Am^{241} on the valency state of americium in the aqueous solution have found that radiation-chemical reduction of AmO_2^{++} ions in a considerable degree is dependent on acidity of the solution as well as on the nature of the acid. For example, in the concentrated solution of perchloric acid the yield G (AmO_2^{++}) is appreciably lower than that in diluted solutions. The reduction of NpO_2^{++} ions in aqueous solutions induced by electron radiation (54) is also dependent on the factors mentioned above. It is of interest that, from the radiation-chemical point of view, the pentavalent neptunium is more stable than other valency states.

Radiation electrochemical processes in aqueous solutions have been an object of several works of soviet authors. N. A. Bakh et al. (22, 55) have examined change of oxidation-reduction potential of several compounds in aqueous solutions under action of ionizing radiation. Extensive investigations of radiation electrochemical processes have been carried out by V. I. Veselovsky and collab. (56-61). In the works of the latter authors it has been discovered that the potential of the platinum electrode in irradiated 0.8 N sulfuric acid solution saturated with nitrogen reaches a value closely approximating the reversible hydrogen potential and the potential of the gold electrode becomes equal to ~0.95 volt.

D. V. Kokoulina, P. I. Dolin and A. N. Frumkin (62), examining the behaviour of a smooth platinum electrode in a solution of sulfuric acid in wide range of doses absorbed and dose rates, have proved that the potential of the platinum electrode in irradiated 0.8 N sulfuric acid is controlled by the molecular radiolysis products of water accumulating in solution, i.e. by hydrogen and hydrogen peroxide. The radical products of radiolysis in this case do not play any appreciable part in potential establishment on electrode. A similar conclusion has been drawn by S. D. Levina and T. V. Kalish (63) from an examination of the behaviour of a nickel electrode under irradiation. Examining the oxidation-reduction reaction $Fe^{++} \longrightarrow Fe^{+++}$ under irradiation P. I. Dolin and V. I. Duzhenkov

(64) have proved the potential possibility of utilizing the products of oxidation and reduction in aqueous solutions for the purpose of transforming energy of radiation into electrical energy. In other words, the possibility of constructing radiation-galvanic cell has been proved. Another solution to this problem has been stated by V. I. Veselovsky et al. (59). They have employed the Pt and Au electrodes having selective properties with respect to oxidizing and reducing agents formed in solutions under irradiation.

There are a number of soviet works examining the influence of ionizing radiation upon the corrosion behaviour of metals in various media. N. D. Tomashov, A. V. Byalobzhesky et al. (65) have studied the effects of electron radiation on corrosion of iron, stainless steel and aluminium in sodium chloride solutions. A. V. Byalobzhesky (66, 67) has examined corrosion of metals under irradiation in air. The corrosion of several metals under irradiation (by fast electron beam, γ-rays of Co^{60}, X-rays) has been found by him to be appreciably accelerated by ionizing radiation. The metals examined can be arranged in the following sequence: iron - copper - zinc - aluminium, the corrosion stability increasing. It has been suggested in the works mentioned above that the corrosion intensification under irradiation is caused by formation of radiolysis products of oxygen, water and nitrogen in the air.

I. L. Rozenfeld and E. K. Oshe (68, 69) have examined the effects of electron radiation on electrochemical activity in various media of zirconium and titanium covered with oxide films having semi-conductor properties. Diminution of anode and cathode reaction overvoltage and increase of rate of these reactions have been found. The effect discovered is reversible: stopping of irradiation leads to return of overvoltage and rates of anode and cathode reactions to values closely approximating to original ones. Another phenomenon of interest discovered by the authors, is the fact that under irradiation, behaviour of metals covered with semi-conductor films of p-type and of n-type with respect to the anode process is quite different. With respect to the cathode reaction such a difference is not observed.

The corrosion behaviour of several metals under irradiation has also been studied by Ya. M. Kolotyrkin et al. (41, 70). For example (41), they have investigated the effects of γ-radiation of Co^{60} on electrochemical properties and corrosion of steel, nickel and platinum in sulfuric acid. It was established, in the case of steel and nickel, that the effect of irradiation is equivalent to anode polarization. The authors have confirmed the conclusion by V. I. Veselovsky with collabor. (56-61) about establishment in sulfuric acid the platinum electrode potential closely approximating a potential of reversible hydrogen electrode.

3. Radiation chemistry of simple inorganic molecules

A number of works by soviet authors are dedicated to the study of radiation-chemical reactions of simple inorganic molecules. Attention to these investigations has been attracted, first of all, owing to the fact that the examinations of such reactions allows, more successfully than in cases of other compounds, to correlate the yields and kinetics with ionization and excitation potentials, dissociation energy and other parameters of irradiated material as well as to study the effect of phase state on radiolysis and to correlate radiation-chemical and photochemical processes.

The most complete investigation in this topic accomplished by soviet chemists is radiation-chemical oxidation of nitrogen with the oxygen. S. Ya. Pshezhetsky and M. T. Dmitriev (71, 72) have examined the kinetics and mechanism of oxidation of nitrogen under the action of electron impact. Nitrogen pressure has been varied from 10^2 to 10^{-3} mm Hg, electron energy - from units of electron-volts to 200 Kev. Formation of N_2^+-ions appears to be an intermediate stage of the reaction. Kinetics of the reaction are described by an equation of the second order, activation energy being in the range 2-7 kcal/mol. Later, M. T. Dmitriev and S. Ya. Pshezhetsky (73) have carried out work on oxidation of nitrogen induced by γ-radiation of Co^{60} under pressures up to 150 atm. and at temperatures 15-25° and at 150°C. It has been observed that increasing of pressure from 1 mm Hg to 760 mm Hg lowers the oxidation reaction yield, but on further increasing the pressure the yield increases, reaching the magnitude of 5-6 molecules of NO_2 per 100 ev at 150 atm. The yield of N_2O at 3-50 atm and at 150°C is 2.5-3.5 mol/100 ev. The dependence of the reaction rate on composition of mixture obeys an equation of the second order. A deviation from the equation of the second order has been observed for the dependence of reaction rate and yield on the pressure, because of recombination of ions formed under irradiation.

Recently M. T. Dmitriev and S. Ya. Pshezhetsky (74) have examined the transformation occurring in nitrogen dissolved in water under action of γ-radiation of Co^{60} and a beam of fast electrons. It has been found that nitrogen dissolved in water under irradiation is fixed in the form of nitrite, nitrate and ammonia. The yield of the reaction is dependent on a composition of mixture of gas dissolved and its pressure. For instance, the yield of nitrogen fixed is 0.09-0.18 at 1 atm and 1.0-1.4 atoms at 150 atm per 100 electronvolts of radiation energy absorbed.

S. Ya. Pshezhetsky et al. (75, 76) have also studied the formation of ozone in liquid and gaseous oxygen under action of γ-radiation of Co^{60} and fast electron stream. Excited molecules of oxygen have been proved to play an important role in the reaction. The radiation-chemical yield of ozone is 12-15 molecules/100 ev in the case of liquid phase and 1.5 molecules/ 100 ev for the gas.

Hydrazine is formed under the action of a fast electron beam on liquified ammonia (77). The latter process is characterized by stationary hydrazine concentration owing to the equilibrium between rates of direct and reverse reactions, the yield being 1.0-1.2 molecules/100 ev.

Also studied have been the kinetics of hydrogen peroxide decomposition depending on its concentration in aqueous solution under action of γ-radiation of Co^{60}, ultraviolet light as well as the analogous dependence for the rate of the thermal decomposition (78). The rate of the reaction as the concentration increases has been found to have always a maximum. It has also been observed that the rate of the radiation-chemical reaction is proportional to the square root of radiation intensity. The activation energy of the radiation-chemical reaction is 6.5 kcal/mol, that of the photochemical reaction being 8-9 kcal/mol. The yield of the radiation-chemical reaction is dependent on temperature. Dependence of a degree of electrolytic dissociation of HO_2-radicals on the concentration of the solution is proposed in the paper for explanation of kinetics of the reaction of H_2O_2 decomposition.

Several papers of soviet authors deal with investigation of effects of ionizing radiation on solid substances.

V. I. Spitsyn et al. (79) have examined decomposition of solid complex compounds of platinum under the action of electron radiation. In these cases formation of free metallic platinum was sometimes observed. The magnitudes of the initial yield of metal are represented in Table 1. The data of the table show that a degree of decomposition of the complexes is dependent on the nature of the salt and space isomerism. For instance, trans- $[Pt\ (NH_3)_2\ Cl_2]$ has lower radiation-chemical stability, than that of the cis-isomer. As is obvious from Fig. 5 and Fig. 6, the degree of decomposition of the complex salts remains unchanged at high integral irradiation doses. In these conditions the process of re-oxidation of free metallic platinum by atomic chlorine brought about with radiation-chemical decomposition of the compounds concerned has apparently a significant part.

Table 1. The initial yields of free metallic platinum on irradiation of complex compounds

Compound	Initial G (Pt), atom/100 ev.
$K_2[PtCl_4]$	0.018
$(NH_4)_2[PtCl_4]$	0.143
$(NH_4)_2[PtCl_6]$	0.090
$[Pt(NH_3)_4]Cl_2$	0.047
$[Pt(NH_3)_2Cl_2]$-cis	0.036
$[Pt(NH_3)_2Cl_2]$-trans	0.338

M. A. Proskurnin et al. have investigated the effect of γ-radiation of Co^{60} on solid $NaNO_3$, $KClO_3$ and $KClO_4$ (80-82), as well as on crystalline hydrates of nitrate salts (83). An interesting paper (83) describes the effect of dose rate of γ-radiation of Co^{60} in the region of $0.2.10^{16}$ to $4.1.10^{16}$ ev/cm^3sec on the radiolysis product yields of several crystalline hydrates of nitrate salts. It has been proved that a minimum in the curve expressing the dependence of G (NO_2^-) upon dose rate is a characteristic feature for all crystalline hydrates examined, the position of the minimum being determined by the nature of the cation. The crystalline hydrates are more

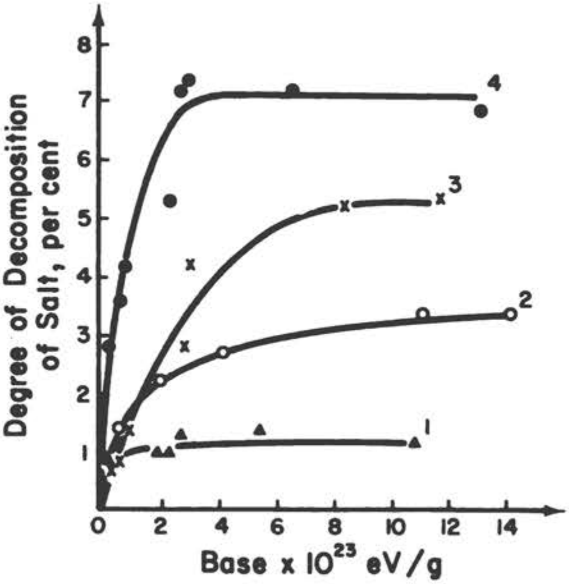


Fig. 5. Decomposition of complex salts of platinum under the action of high energy electron beams depending on integral dose.

1 - $(NH_4)_2[Pt\ Cl_6]$
2 - $[Pt(NH_3)_4]Cl_2$
3 - cis-$[Pt(NH_3)_2Cl_2]$
4 - trans-$[Pt(NH_3)_2\ Cl_2]$

Temperature of the experiments was 145-150° C.

sensitive to the action of γ-radiation than the corresponding unhydrous salts.

V. V. Boldyrev et al. (84) have considered the effect of preliminary irradiation on the rate of thermal decomposition of silver oxalate contaminated with cadmium. The preliminary irradiation with γ-rays of Co^{60} brings about an intensive

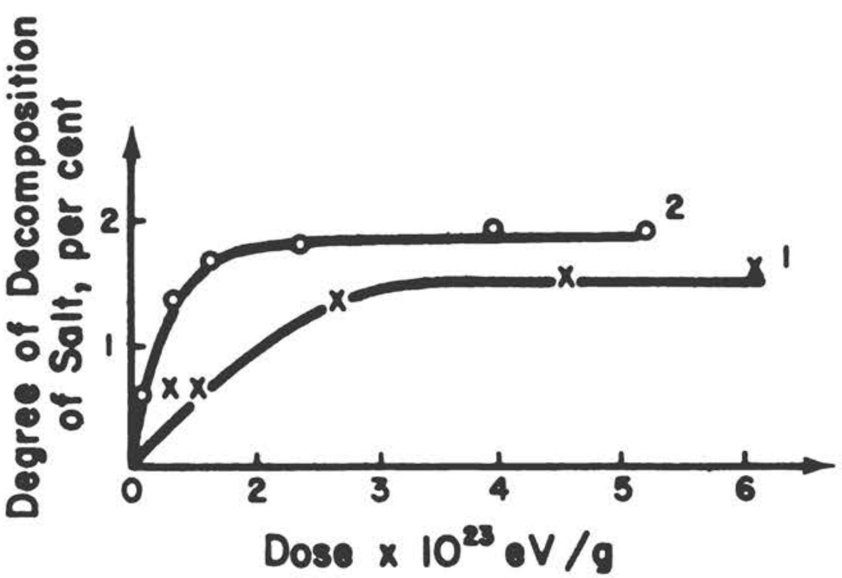


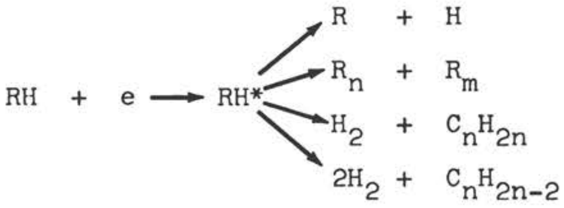
Fig. 6. Decomposition of potassium chloroplatinate (1) and ammonium chloroplatinate (2) under the action of high energy electron beams. Temperature of the experiments was 90-95° C.

acceleration of the subsequent thermal decomposition of pure silver oxalate. Thermal decomposition of the salt containing traces of cadmium is accelerated, too, but in a considerably smaller degree. In the opinion of the authors the phenomenon is caused by the formation in the presence of cadmium in crystal lattice additional number of cation vacancies, which can trap positive holes or argentum cations from interstitialcies.

4. Radiation chemistry of organic compounds

The reactions of organic compounds induced by ionizing radiation are objects of research work of a number of soviet investigators. The works are carrying on in several directions.

A. V. Topchiev and L. S. Polak with collaborators (85-92) are carrying out the systematic investigation of the effects of γ-radiation of Co^{60} and of fast electron beams on hydrocarbons in gaseous, liquid and solid phases. Based on experimental data the following possible types of initial radiolysis reaction of normal alkanes have been suggested in their papers.



$$RH + e \longrightarrow RH^* \longrightarrow \begin{cases} R + H \\ R_n + R_m \\ H_2 + C_nH_{2n} \\ 2H_2 + C_nH_{2n-2} \end{cases}$$

Examination of ESR-spectra of n-heptane irradiated at 77°K in frozen state indicated the occurrence of free alkyl radicals and also of H-atoms but in a smaller number. It has been proved that these radicals can be kept at low temperatures over a long period of time.

It has been found by the authors mentioned above as well as by foreign authors that the total yield of the radiolysis products of hydrocarbons at room temperature is about 10 molecules/100 ev, the predominant process being dehydrogenation. The examination of the radiolysis of n-heptane is the most detailed. On irradiation of n-heptane under ordinary conditions the gaseous radiolysis products contain about 80% of hydrogen. The remaining 20% includes saturated and unsaturated hydrocarbons.

In the series of soviet investigations in radiation chemistry of hydrocarbons those of radiation thermal cracking of hydrocarbons are of a significant interest (90-92). It has been found that on simultaneous action of radiation and heat the chain reaction of cracking occurs, initiation of the reaction being caused by radiation, while propagation of the reaction is maintained on account of heat energy. For instance, as one can see in Fig. 7, irradiation of n-heptane at elevated temperatures leads to the sharp increasing of yields of hydrocarbon products of radiolysis. Moreover, among the products of radiolysis an increase in unsaturated hydrocarbon content is noted (Fig. 8). One can suppose that the radiation thermal cracking of hydrocarbons should be a promising method as regards to uses of nuclear radiation in the practice purposes.

Another branch of radiation chemistry of organic compounds developed by soviet scientists is the study of radiation induced oxidation processes in organic systems. N. A. Bakh with collabor. (93-99) are carrying on the most methodical research in this topic, under utilization of diverse types of radiation: X-rays, γ-radiation of Co^{60}, fast electrons, and mixed radiation of a nuclear reactor. These authors are first to have found (93-94) that under irradiation of liquid hydrocarbons (heptane, isooctane, benzene, cyclohexane, etc.) saturated with oxygen, the oxidation of the hydrocarbons at room temperature occurs generating peroxides, carbonyl compounds, alcohols, acids, etc., formation of these compounds being simultaneous right from start of irradiation. In the case of hydrocarbons under ordinary conditions the reaction

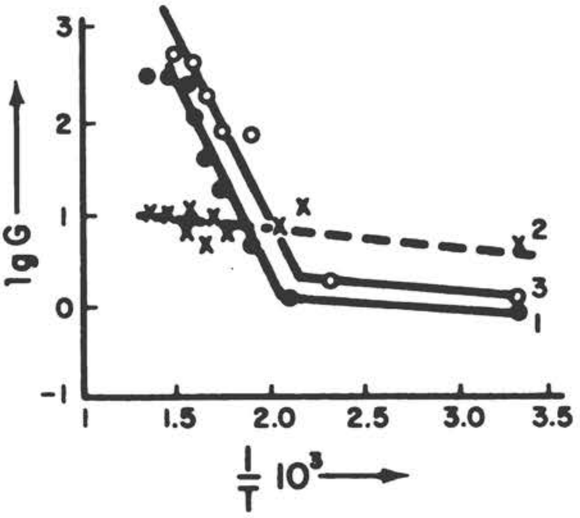


Fig. 7. The dependence of logarithm of radiation-chemical yield of methan (1), hydrogen (2) and hydrocarbon fraction C_2-C_6 (3) on inverse temperature of the radiation thermal cracking.

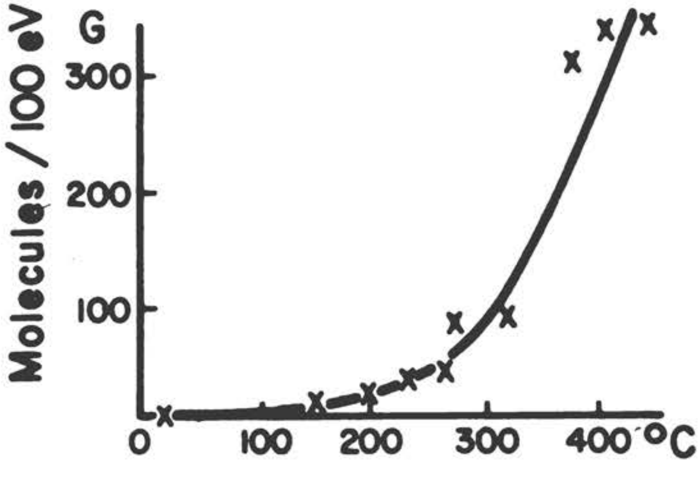
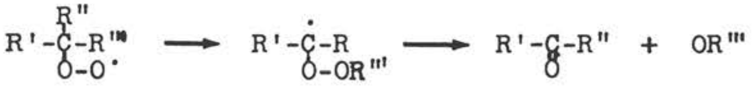


Fig. 8. The dependence of radiation-chemical yield of liquid olefins upon temperature of the radiation thermal cracking.

of oxidation is not a chain reaction. Ethyl alcohol and acetone, molecules which contain more movable atoms of hydrogen are oxidized in the chain mechanism with short chain. The following scheme suggested by N. A. Bakh, for explanation of radiation induced oxidation is based on the supposition that peroxide radicals can be formed by addition of oxygen molecules to free hydrocarbon radicals. The simultaneous formation of the radiolysis products is caused by occurrence of some parallel reactions of the peroxide radicals of one type or by simultaneous formation of the various peroxide radicals:

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2$$

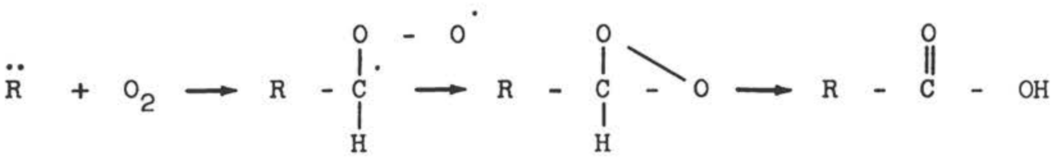
$$R\dot{O}_2 + RH \longrightarrow ROOH + \dot{R}$$



$$R'\text{-}\underset{O\text{-}O^{\bullet}}{\overset{R''}{C}}\text{-}R''' \longrightarrow R'\text{-}\underset{O\text{-}OR'''}{\dot{C}}\text{-}R \longrightarrow R'\text{-}\underset{O}{C}\text{-}R'' + OR'''$$

$$R\dot{O}_2 + R' \longrightarrow ROOR'$$

Biradical $\ddot{R}$, which can also arise under irradiation of hydrocarbon, interacting with oxygen gives a molecule of acid:



Oxidation of methane by oxygen at room temperature under action of fast electron beam has furthermore been studied by B. M. Mikhailov et al. (100-102). They also have not observed any chain reaction of oxidation.

N. A. Bakh as well as M. A. Proskurnin are carrying out investigations of radiation induced oxidation of organic compounds in aqueous solutions. In this case oxidation is mainly caused by interaction of radiolysis products of solvent with dissolved substances. Hence the oxidation can here take place even in the absence of molecular oxygen.

M. A. Proskurnin et al. (103-104) have conducted a detailed examination of radiation-chemical oxidation of benzene into phenol in aqueous solution. They have observed an interesting phenomenon: the yield of phenol in the presence of Fe^{++}-ions can increase 3 times as against the ordinary yield and amounts 6 molecules/100 ev. Radiation induced oxidation of chlorbenzene in aqueous solutions has also been examined (105). It has been proved that hydrolysis of chlorbenzene plays an important part in the radiolysis.

N. A. Bakh et al. (106) have investigated oxidation of ethyl and isopropyl ether in aqueous solutions under action of X-rays and fast electron beam. In the presence of oxygen the process of their oxidation proceeds by a chain mechanism. Products of the reaction in both cases are peroxides (the yield is about 20 molecules/100 ev), carbonyl compounds (the yield is about 25 molecules/100 ev), alcohols and acids.

At high temperatures, as it has been shown by N. M. Emanuel (107) and M. A. Proskurnin et al. (108, 109), chain oxidation of hydrocarbons under action of radiation takes place. For instance, it has been observed that under action of γ-radiation paraffin in the presence of oxygen is effectively oxidized at 127-130°C giving fatty acids. The process of oxidation proceeds by the degenerated chain-branching mechanism.

Recently N. A. Bakh and Tung Tyan'-chzhen' (110) have examined the temperature dependence of radiation-chemical oxidation of n-heptane and n-nonane. For both hydrocarbons studied there are two regions of temperature dependence of the yield of oxidation products. At temperatures below 70°C small yields and independence on temperature are observed. At temperatures above 70° the yield of radiolysis products sharply increases with temperature, reaching in the case of peroxides the value of 30-40 molecules/100 ev. In the case of radiation induced oxidation of n-alkanes as it has been shown in the paper mentioned, interference of chain and ordinary reaction mechanism is a distinctive feature. The temperature, at which the chain reaction are initiated, is dependent on the nature of irradiated compound.

A number of soviet scientists are studying the effects of ionizing radiation on mixtures of organic compounds. The work of Kh. S. Bagdasarian with collabor. (111-113) is of a considerable theoretical interest. Examining γ-radiation induced decomposition of benzoyl peroxides in various solvents the authors mentioned above have found that in benzene solutions effective transfer of excitation energy from benzene molecules to peroxide molecules occurs, increasing in a significant degree the radiation chemical yield of its decay. For the reaction studied excitation energy transfer is observed if molecules of both the constituents of the solution have aromatic groups. For example, in cyclohexane and ethyl acetate solutions the energy transfer from solvent does not occur, and a chain reaction of decomposition of peroxide is induced by radicals formed under irradiation of solvents. However any simple correlation between structure of molecules and its ability to accept the excitation energy does not exist (113). For example, azobenzene does not accept the excitation energy, although its molecules contain two phenyl rings conjugated with double bond. Some compounds being active acceptors of the energy are negligibly capable or uncapable at all to use the energy for chemical transformation. For instance, such a compound is phenylazotriphenyl methane, which does not dissociate on radicals, under action of excitation energy accepted in spite of the fact that this reaction occurs easily under the action of heat.

In the recent paper of Kh. S. Bagdasarian et al. (114) examination of radiolysis of diluted benzene solutions of organic disulphides containing aromatic and aliphatic substituents has been described. Due to the radiation energy transfer from the solvent to the dissolved compound, the yields of decomposition of disulphides have been found to be sufficiently higher than the yield being expected in the case when all the energy absorbed by them would be spent completely for their decomposition. The energy transfer efficiency has been found in the work referred to be dependent on the nature of the disulphide. Thus, diphenyldisulphide and dibenzyldisulphide are approximately identical energy acceptors, while the accepting capacity of dibenzoyldisulphide is half of that of the former.

Aliphatic disulphides (diethyldisulphide, dioctyldisulphide) manifest more low decomposition yields than those of aromatic disulphides, due to the considerably smaller intermolecular energy transfer efficiency.

A number of papers have been published by soviet authors, dealing with radiation-chemical halogenation, amidation, etc. P. V. Zimakov et al. (115) have examined effects of γ-radiation of Co^{60} on the chlorination reaction of benzene in the temperature region from -80 to +40°C. The radiation-chemical chlorination of benzene has been found to proceed with the yield of 400,000 molecules/100 ev, the resulting material having elevated content of high-toxical γ-isomer of hexachlorcyclohexane in comparison with industrial product obtained by photochemical method. Recently the advantages of radiation-induced chlorination of benzene were confirmed by the same authors. However the elevated content of γ-isomer was not obtained.

The effects of ionizing radiation on mixtures of benzene-ammonia, benzene-carbon tetrachloride, and benzene-carbon tetrachloride with compounds containing fluorine have been examined by A. M. Zimin with collabor. (116-118). In the mixture of benzene and ammonia under γ-irradiation aniline with a small yield is formed. In the case of the benzene-carbon tetrachloride system formation of monochlorebenzotrichloride has been observed (parallel with some other radiolysis products). In the mixtures of CCl_4 with inorganic fluorides and of benzene with simplest fluorcarbons fluorination of CCl_4 and of benzene takes place.

P. V. Dzhagatspanian et al. (119) have studied chlorination of silicon-organic monomers and ploymers under effects of γ-radiation. In another paper of the authors mentioned (120) radiation-chemical sulphochlorination and sulphooxidation of paraffins as well as some polymers are described.

Researches on working up of radiation-chemical methods of organic synthesis are carried out in this country. K. A. Kocheshkov et al. (121) have proposed the radiation-chemical method of preparation of tin-organic compounds. V. I. Spitsyn et al. (122) have worked out radiation-chemical synthesis of butyl ether of phosphonitryl chloride. The reaction proceeds with a good yield under action of fast electron beam on solution of phosphonitryl chloride in n-butyl alcohol.

Radiation-chemical transformations in dyes and substances of biochemical interest are also being studied by soviet chemists. I. V. Vereschinsky (123) has examined the synthesis and transformations of leuco-compounds of the dyes under action of γ-radiation of Co^{60} as well as the effects of γ-radiation on synthesis of indophenol (124). In a number of soviet papers (125-128) the radiolysis of methylene blue in aqueous solution is described. M. A. Proskurnin et al. (129) examined radiolytic decoloration of indigo carmine solutions. A large number of investigations deal with the effects of ionizing radiation on substances of biological interest, i.e. proteins (130), amino-acids (131), carbohydrates (132), animal fats (133), etc. Radiolysis of protoporphyrin has been examined by I. V. Vereschinsky (134).

5. Radiation polymerization

Radiation polymerization, at present, ranks rather high among the problems to be solved for the uses of ionizing radiation in practice. This is called forth by the fact that in the majority of cases the radiation induced polymerization as it has been shown in a number of papers including some papers of soviet authors (135), proceeds by a chain mechanism, the process being initiated by free radicals arising under irradiation of the monomer.

Researches in radiation polymerization are carried out in many countries. In the USSR the work in this field has been done by S. S. Medvedev (135, 136), Kh. S. Bagdasarian (137, 138), A. D. Abkin (139-141), B. L. Tsetlin (142) and other soviet investigators.

Among the recent investigations on this topic that of B. L. Tsetlin, V. A. Sergeev, S. R. Rafikov, V. V. Korshak, P. Ya. Glasunov and L. D. Bubis (142), concerning radiation-chemical polymerization of methylmetacrylate, is of a considerable theoretical and practical interest. In the presence of air the methylmetacrylate has been found not to be polymerized under action of ionizing radiation. However, spontaneous polymerization of the irradiated material proceeds at room and lower temperatures to the high degree of the conversion, after the access of the material to ambient air has been stopped. Investigations of the polymerization kinetics of irradiation at various temperatures, indicated that, in the first degree of approximation, the process by its character is identical to the polymerization process of peroxide type and other types of radical polymerization. In the opinion of the authors of the paper cited, the polymerization process is initiated by products of radiation-chemical oxidation of methylmetacrylate (probably peroxides formed by interaction of primary free radicals with oxygen). Being highly active these products create the possibility that low-temperature polymerization can be executed. The feature of interest is the fact the curves representing polymerization kinetics are in this case more smooth in comparison with those in the case of polymerization by benzoyl peroxide. The "gel-effect" in the processes described takes place when a considerably higher degree of conversion is achieved and the ratio of the maximum reaction rate in the self-acceleration stage to the initial rate is of smaller value. The curves representing the dependence of ratio of polymerization rate in a given moment to the initial rate upon relative duration of the process are shown in Fig. 9.

Recently the paper of S. S. Medvedev, A. D. Abkin with collab. (143) about polymerization of ethylene under γ-radiation of Co^{60} was published. In this work the rate of radiation polymerization of ethylene in solution and in gaseous phase under various pressures (concentrations), as well as some properties of polymers formed have been examined. At a pressure of 50 atm, temperature of 25°C and dose rate of 98 roentgen/sec, polymerization of ethylene in heptane, cyclohexane, methyl alcohol and acetone proceeds with a rate 10

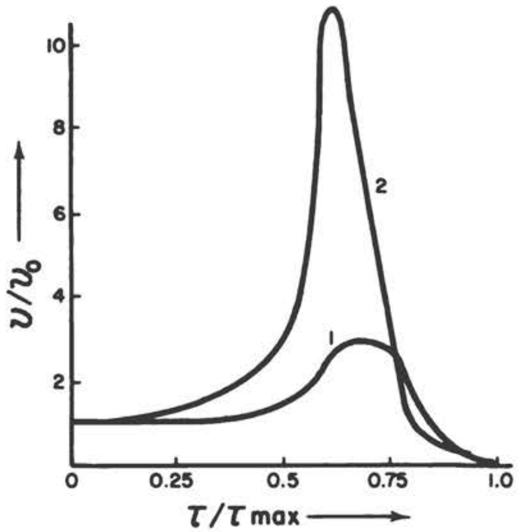


Fig. 9. The influence of a mode of initiation on the shape of the kinetics curves of polymerization of methyl methacrylate (temperature 60° C):

1 - polymerization of pre-irradiated monomer (dose 4.10^{20} eV/cm^3)

2 - polymerization of methyl methacrylate in presence of benzoyl peroxide (0.01 %).

v/v_0 is the ratio of the polymerization rate in a given moment to the initial rate;

τ/τ_{max} is relative duration of polymerization process.

times exceeding the rate of the polymerization in gaseous phase at the same pressure. In carbon tetrachloride tetrachloralkanes with various molecular weight are formed. At the initial stages the process proceeds with acceleration, later the rate of the process being constant. The rate of the process is proportional to the irradiation dose rate in the power 0.3, while the radiation yield is inversely proportional to the dose rate in the power 0.7. The resulting polyethylene possesses higher density (0.945-0.975 g/cm^3) and crystallinity than the high pressure polyethylene. Tensile strength of the polyethylene prepared by radiation-chemical method differs little from that of the high pressure polyethylene.

Kh. S. Bagdasarian, V. V. Voevodsky et al. (138) have carried out investigations of graft-polymerization with irradiated teflon. For elucidation of the mechanism of the process a method of electron spin resonance has been employed.

Kh. U. Usmanov, U. N. Musaev, R. S. Tillaev (144) have investigated the radiation-chemical method of preparing graft-copolymers in the systems polystyrene-acrylnitryl and perchlorvinyl-acrylnitryl. It has been observed in the case of polystyrene and acrylnitryl that the reaction proceeds in a polystyrene film swollen in acrylnitryl under radiation up to dose 1.10^6-4.10^6 roentgen. Preparation of graft-copolymers on the basis of perchlorvinyl and acrylnitryl was accomplished by irradiation of a perchlorvinyl film (in presence of air) with the consequent treatment with acrylnitryl.

As it has been mentioned, radiation polymerization in most cases proceeds by a free radical mechanism. However, recently it has been established that under certain conditions (e.g. at low temperature) polymerization under action of ionizing radiation can also proceed by carbonium-ion mechanism. Thus A. D. Abkin et al. (139, 141) have demonstrated this fact by copolymerization in the systems: isobutylene-vinylidene chloride, styrene-methyl methacrylate, isobutylene-styrene. Recently (140, 141) results indicative of the possibility for the reaction to proceed by a carbanion mechanism have been obtained. Acrylnitryl, which molecules contain an electronegative group, is polymerized under the action of γ-radiation of Co^{60} in solvents containing nucleofilic substituents (e.g. triethylamine or dimethylformamide) but is not polymerized in the solvents containing electrofilic group (e.g. ethyl chloride). On the other hand, in ethyl chloride styrene is polymerized. In Table 2 the data obtained by A. D. Abkin and collabor. are presented concerning polymerization of acrylnitryl in various solvents at temperature -78°C under effects of γ-radiation.

Table 2

Monomer	Concentration of monomer, mol/l	Polymerization rate (mol/l x 10^5) in:			
		ethyl chloride	dimethyl formamide	triethylamine	in block
Styrene	2.0	1.95	no polymerization		
Acrylnitryl	3.5	no polymerization	0.97	0.67	0.21

If copolymerization of acrylnitryl and styrene in dimethylformamide solution is carried out at -78°C, the resulting copolymers have been found by the authors mentioned, to be highly enriched by nitryl component in comparison with the original mixture. All these data are indicative of the possibility to realize the carbanion mechanism of polymerization by the action of ionizing radiations.

Investigation of employment of ionizing radiation for preparation of inorganic polymers are begun by soviet scientists. Thus, V. I. Spitsyn et al. (145) have demonstrated the potential possibility of polymerization of phosphonitryl chloride under electron radiation. It is of interest that in this case polymerization proceeds only in the presence of oxygen.

6. Effects of ionizing radiation on polymers

In the USSR the first systematic investigations of effects of radiation on polymer materials were carried out by V. A. Kargin with collab. (146-149) concerning, mainly, change of thermo-mechanical properties of irradiated materials. At present investigations in this field are being carried out by a number of soviet scientists (S. S. Medvedev, V. L. Karpov, Yu. S. Lasurkin, B. L. Tsetlin, N. A. Slovokhotova, A. B. Taubman).

V. L. Karpov et al. (150, 151) studied the effect of radiation on various polymer substances*. They employed radiation of different kinds including α- and β-radiation of radon and products of its disintegration, γ-radiation of Co^{60}, fast electron beams, mixed irradiation of nuclear reactor. It was found that all polymers can be subdivided into two principal groups. The polymers of the first group are characterized by predominance of destruction processes, i.e. rupture of polymer

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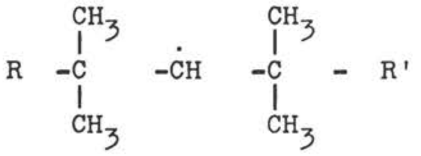
*Researches in the field of radiation chemistry of polymers had been begun by V. L. Karpov in 1947.

chain. The polymers, in which under action of radiation process of cross-linking predominates, i.e. formation of chemical bonds between macromolecules, constitutes the second group.

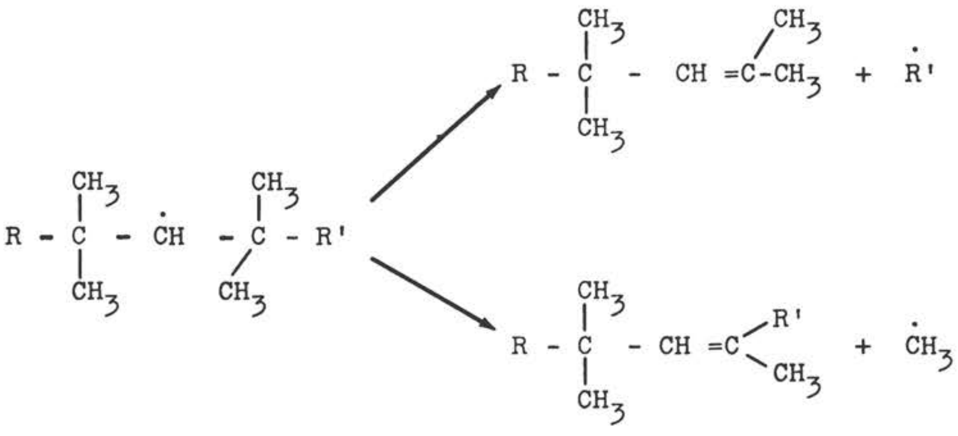
Gas evolution of polymers under irradiation was studied by V. L. Karpov et al. (150, 152) and some conclusions concerning mechanism of radiation-chemical reaction in polymers were deduced. In the case of cross-linking polymers the major part of the gas evolved is hydrogen. Thus for instance, under irradiation of polyethylene the gas evolved contains 95.5% of hydrogen. This can be confirmation of the suggestion that the cross-linking process passes through intermediate stage of formation free radicals by rupture of C-H bonds. Destruction of polymers is observed in all the cases when the main chain of macromolecule contains quaternary carbon atoms. Under irradiation of such polymers the evolving gas is impoverished in hydrogen and contains considerable amount of compounds resulting from detaching of side groups at quaternary carbon atom.

In their investigations V. L. Karpov and N. A. Slovokhotova (153-155) employed widely optical methods. By this technique it has been found in the case of polyethylene that irradiation results in gradual disappearance of vinylidene double bonds, which were present in the original material in a small amount, and formation of new double bonds of the trans-vinyl type (mainly conjugated). Formation of the double bonds is also observed in the case of destructing polymers. In polyisobutylene formation of double bonds proceeds in all probability, by the following mechanism. By H-atom abstraction from secondary carbon atom the radical of the following type arises:



$$R-\overset{CH_3}{\underset{CH_3}{C}}-\dot{C}H-\overset{CH_3}{\underset{CH_3}{C}}-R'$$

Because of steric hindrance this radical cannot form cross-link, and undergoes further destruction:



Examination of infra-red spectra has helped to discover the peculiarities of interaction of irradiation polymers with oxygen of the air. This process has been found to bring about formation of oxi-groups in the polymer. Another phenomenon of interest observed by V. L. Karpov et al. (150, 152, 156) is destroying of crystallinity in polymers under the effects of γ-radiation of Co^{60} or fast electrons. These processes were observed in the cases of polyethylene, guttapercha, co-polymer of vinyl chloride and vinylidene chloride, polytetrafluorethylene and some other crystalline polymers.

V. L. Karpov, L. A. Blumenfeld et al. (157), by means of measurements of infra-red spectra, absorption spectra and electron spin resonance spectra of irradiated polyvinylchloride have proved that the profound changes observed in this material under electron irradiation consist chiefly in splitting off hydrogen chloride and formation of double bond. In the opinion of the authors, free radicals are responsible for change of colour in polyvinylchloride under effects of radiation. Their availability in the irradiated polymer has been proved by the electron spin resonance method, their concentration being decreased with time progression. This decreasing is caused by recombination of the radicals in evacuated polymer and by interaction of the radicals with oxygen, resulting in the formation of peroxide radicals if oxygen is available.

The papers of A. B. Taubman et al. (158, 159) deal with problems of elucidating peculiarities of radiation destruction of polymers. They have examined the effects of electron radiation and high temperature on destruction of polytetrafluorethylene, polymethylmethacrylate and polyethylene. The authors have obtained sharp changes in rate of gas evolution under irradiation in narrow temperature regions where melting (softening) of polymers is observed.

The phenomena of cross-linking in polymers has earned the attention of soviet chemists since due to this process most polymers acquire valuable properties. The mechanism of cross-linking in polyethylene has been examined by S. S.

Medvedev et al. (160, 161). The temperature dependence of cross-linking in this material implies that cross-linking is the result of simultaneous detachment of two hydrogen atoms in a single primary act from two adjacent macromolecules.

V. V. Voevodsky et al. (162) have examined by means of ESR-method the formation of free radicals in irradiated polyethylene. Radicals of two kinds (of alkyl and allyl types) have been observed in irradiated polyethylene. The stability of these radicals is different implying a different mechanism of their recombination. In the opinion of the authors the recombination of radicals accumulated in the course of irradiation must play an important part in the process of cross-linking in polyethylene.

In the recently published paper of S. S. Medvedev et al. (163) conclusions of considerable interest have been deduced concerning a protection effect mechanism of benzene rings in the radiolysis of polystyrene. Polystyrene is known to have a high radiation stability: in the case of polyethylene formation of a single cross-link requires 25-35 ev, while in the case of polystyrene 3000-5000 ev are necessary. Based on investigations of radiolysis of toluene* labelled by deuterium the authors have concluded that the high radiation stability of polystyrene is largely caused by a disproportionation reaction of primary radicals with cyclohexadienyl type radicals

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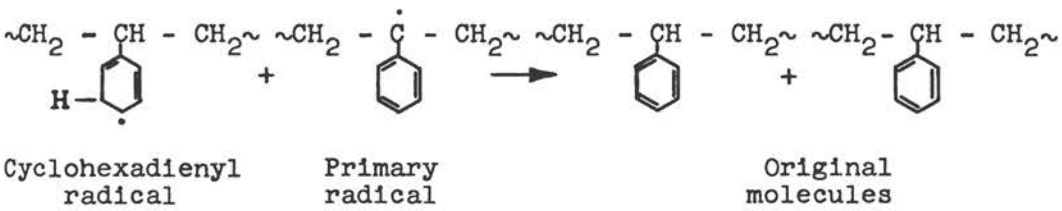
*At the radiolysis of toluene the radicals formed have a structure similar to that of the radicals arising in polystyrene under irradiation.

arising in the polymer under irradiation:



Yu. S. Lazurkin and G. P. Ushakov (164) have examined the radiation cross-linking of polydimethylsiloxane. The vulcanizates resulting demonstrate more high strength and resistance to freezing than that obtained by conventional methods. Radiation-chemical cross-linking (vulcanization) of resins is an object of research of A. S. Kuzminsky, V. L. Karpov and T. S. Nikitina (165, 166). Radiation vulcanization of different resins has been established by the authors and can be a method of preparation of rubbers with new valuable properties.

S. A. Pavlova, S. R. Rafikov, B. L. Tsetlin (167) have obtained experimental evidence that the two opposite reactions, i.e. reaction of cross-linking and that of destruction under action of radiation on polyamides proceed simultaneously. The authors have accomplished combined investigations including the change of mechanical properties, as well as the properties of the solutions, the change of molecular weight and molecular weight distribution function of the irradiated material. By this means they have succeeded in distinguishing the two parallel reactions of cross-linking and destruction. However, the cross-linking is a predominant process and vulcanization of polyamide is a final result of irradiation of this material.

Recent investigations of changes in the properties of polymer immediately in the course of their irradiation accomplished by soviet scientists are of a considerable interest. Yu. S. Lazurkin et al. (168) have examined the change of mechanical properties of different polymers in the course of irradiation in a nuclear reactor. Reversible radiation-mechanical effects have been observed to appear in the course of irradiation, i.e. change of mechanical properties appears in the time of irradiation and disappears after irradiation has been stopped. Reversible changes in gas-penetrability of polymers in the time of γ-irradiation have been examined by V. L. Karpov et al. (169). It has been found that when the Co^{60} source of γ-radiation is put in or out the rate of gas diffusion through the polymer undergoes a sharp change, approaching after irradiation the original value, but still remaining slightly higher than the latter.

Ya. M. Varshavsky, G. Ya. Vasiliev, V. L. Karpov, Yu. S. Lazurkin and I. Ýa. Petrov (170) have studied isotope exchange between deuterium gas and different solid polymers in the radiation field of a nuclear reactor to examine whether hydrogen from a gaseous phase can be implanted into polymer molecules in the course of irradiation. Polyethylene and polypropylene have been proved to trap the most hydrogen in comparison with other polymers examined. The rate of isotope exchange is slower in the case of polybutadiene and polystyrene. The authors have suggested that the intrusion of deuterium is caused by reaction of polymer radicals arising under irradiation and deuterium molecules:

$$\dot{R} + D_2 \longrightarrow RD + D$$
$$RH + D \longrightarrow \dot{R} + HD, \text{ and so on.}$$

Uses of the isotope exchange technique in wide scale will, undoubtedly, assist to understand more completely the mechanism of polymer radiolysis.

7. Radiation elementary acts and primary chemical processes

In all chemical transformations in irradiated material secondary electrons, ions, excited molecules and free radicals (including atoms) are involved. The identification of those products is of a significant importance for elucidation of the mechanism of radiation-chemical reactions. This problem is solved by means of mass spectrometry, electron spin resonance, etc.

V. L. Tal'rose and E. L. Frankevich (171) employing mass spectrometry technique to the investigation of products formed under electron impacts in some simple inorganic and organic compounds in gaseous phase, have found that the ion-molecule reactions playing an important part in primary radiation-chemical processes can give excited radicals:

$$M^+ + RH \longrightarrow MH^+ + \dot{R}^*$$
$$M^+ + R'R'' \longrightarrow (MR')^+ + (\dot{R}'')^*$$

This phenomenon has been observed in many processes in vapour phase including $H_2^+ + H_2O \rightarrow H_3O^+ + H$; $CH_4^+ + H_2O \rightarrow H_3O^+ + CH_3$; $C_3H_8 + H_2O^+ \rightarrow H_3O^+ + C_3H_7$, etc.

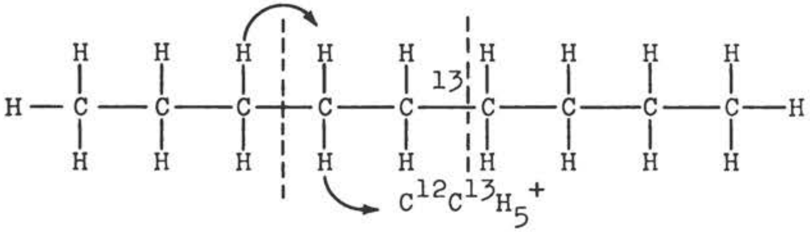
In another paper V. L. Tal'rose (172) has pointed out that formation of different type traps under irradiation (especially in the case of hydrocarbons) can play an important part in radiation chemistry. Under irradiation of saturated hydrocarbons can arise unsaturated compounds and free radicals ionization potentials of which are lower than those of molecules of the original substance. Such compounds and radicals can act as p- and n-traps. Increasing of amount of the traps in condensed phase creates the conditions which favour the principal elementary process consisting in recombination of "plus-minus" pair to be influenced with an adjacent free valence. One of two radicals arising at the recombination can add to this free valence, the probability of the latter process being, practically, equal to the unit in the case of hydrocarbon system.

Of great interest is employment of pulsed irradiation for measurement rate constants of ion-molecule reaction. Combining pulsed irradiation and mass spectrometry technique V. L. Tal'rose and E. L. Frankevich (173) have determined rate constants for the following reactions:

$$CH_4 + CH_4^+ \longrightarrow CH_5^+ + CH_3$$
$$H_2O + H_2O^+ \longrightarrow H_3O^+ + OH$$

At 370°K the rate constant of the former is equal to $11.6.10^{-11}$ cm^3/mol. sec., that of the latter is $8.5.10^{-10}$ cm^3/mol. sec. at 410°K.

N. N. Tunitsky et al. (174-178) are studying dissociation of rather large molecules under electron impacts using mass spectrometry techniques. Examination of mass spectra of halogenated hydrocarbons (174-175) indicated that with increasing of halogen atom quantity in the molecule the per cent of molecular ions in mass spectra decreases. The authors have also found (176, 177) that the most complete agreement of calculated and experimental data take place when approximately equal probability of fragment ion formation from every part of the molecule is supposed. For instance, in the mass spectrum of n-nonane-5-C^{13} ions $C^{13}H_3^+$, $C^{12}C^{13}H_5^+$ and $C_2^{12}C^{13}H_7^+$ have been observed in amounts which are approximately equal to the value which can be calculated proceeding from the assumption mentioned above. Based on analysis of mass spectra the authors have proposed the following scheme of large molecules dissociation:



Quite recently V. L. Tal'rose and E. L. Frankevich (179) have carried out a comparative investigation of induced electrical conductivity and behaviour of free radical in irradiated solid paraffin. They have measured conductivity of paraffin irradiated at 77°K in the time of "annealing". In this case a sort of "flaring-up" of conductivity has been discovered (Fig. 10). This phenomenon appears as follows. At temperatures differing by some dozens of degree from the temperature region where "dark" conductivity takes place, a considerable magnitude of conductivity is observed. On further increasing of temperature the conductivity reduces to "dark" conductivity. The time-temperature region of "flaring-up" is coincident with the region where decreasing of ESR-signal is observed. Based on these data the conclusion has been deduced according to which formation of ions in irradiated solid or liquid material can proceed through formation of free radicals.

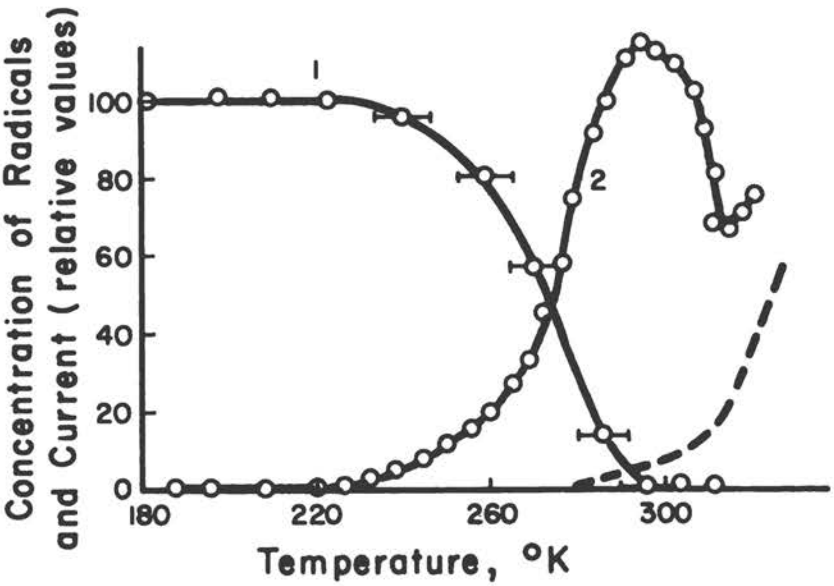
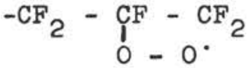


Fig. 10. Variation of radical concentration and electrical conductivity of irradiated paraffin under heating. Heating rate is equal to 22° C/min.

1 - concentration of radicals (in arbitrary units)

2 - relative variation of the current through the sample at 1000 volts potential difference between the electrodes placed inside the sample. Variation of the dark conductivity is indicated with the dotted line.

V. V. Voevodsky et al. (162, 180-185) are carrying out investigation of radicals appearing in radiolysis of organic and inorganic systems using electron spin resonance technique. An apparatus which permits the observation of ESR-spectra in the course of irradiation with fast electrons has been constructed by the authors (162, 180). By means of this apparatus ESR spectra and radical formation kinetics have been studied. The radicals forming under irradiation of teflon in vacuum at low temperature have been found to have a long life-time. In the air they convert peroxide radicals  $-CF_2 - \underset{O - O^{\cdot}}{\underset{|}{CF}} - CF_2 -$ which can be stored at room temperature for some months.

In the case of benzene radicals C_6H_5 and C_6H_7 have been found to form (182):

$$C_6H_6 \rightsquigarrow C_6H_5 + H; \quad C_6H_6 + H \rightarrow C_6H_7$$

In polyphenyls (diphenyl, p-ditolyl, etc.) abstraction of H-atoms and CH_3 - groups situated in para-position with respect to phenyl substituent occurs to form a radical being analogous to C_6H_7.

* * *

In this review we have not discussed some other branches of radiation chemistry developing in the USSR. This paper, for instance, does not contain any description of effects of ionizing radiation on catalysts and semi-conductors, neither does it contain chemical dosimetry or design of radiation sources. Nevertheless, the contents of the review gives an idea of the wide-scale work in the field of radiation chemistry carried out in the USSR.

There is no doubt that in the next years and decades more and more large radiation sources than at present will be available. Elementary particle acceleration technique is going to be improved day by day, power of nuclear reactors is also growing. It becomes then possible to obtain more and more highly active preparates of artificial radioactive isotopes. Energy released by uranium nucleus fission can, undoubtedly, be used in the future for new chemical processes to be put in practice. All those open a bright perspective for radiation chemistry, which is one of the most progressive branches of modern physical chemistry and special chemical engineering.

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THE PROBLEM OF BASICITY OF HETEROPOLY ACIDS AND THE NATURE OF SO-CALLED HIGH-SUBSTITUTION SALTS

By V. I. Spitsyn

The theory of the structure of heteropoly acids suggested by Miolati (1) and Rosenheim (2) requires 6-coordination for the central atoms of their anions (for example, phosphorus or silicon). The addends assumed for the inner sphere are, as a rule, ions of the type of $R_2O_7^{2-}$, where R=Mo or W. For this reason phosphomolybdic acid should be heptabasic, $H_7[P(Mo_2O_7)_6]$, and silicotungstic acid, octabasic, $H_8[Si(W_2O_7)_6]$. Meanwhile, in acid solution, when the heteropoly anions are stable, tri-substituted phosphomolybdates and tetra-substituted silicotungstates usually form, i.e., the basicity of the heteropoly acid practically equals that of the non-metallic acid on which it is based. To confirm the Miolati-Rosenheim theory the existence of high substitution salts of heteropoly acids had to be proved.

Of major importance in this respect was A. Rosenheim and J. Pinsker's communication (3) concerning the preparation of heptasubstituted guanidine phosphomolybdate. By the interaction of phosphomolybdic acid with a calculated amount of a 10 per cent solution of guanidine carbonate they isolated the sparingly soluble tri-substituted salt $(CN_3H_6)_3H_4[P(Mo_2O_7)_6]\cdot 10\ H_2O$. Further addition of guanidine carbonate to a heated suspension of this precipitate transferred the compound into solution, from which a precipitate again separated on cooling. The above authors found the composition of the latter to correspond to the formula $(CN_3H_6)_7[P(Mo_2O_7)_6]\cdot8H_2O$.

As V. I. Spitsyn and K. G. Koneva have shown (4), tri-substituted phosphomolybdates and phosphotungstates of the saturated series exist in the 2.5-2.0 pH range. An insignificant rise in pH (to 3.0-2.7) is enough to cause salts of the 11 series to form (5).

Adding guanidine carbonate to the tri-substituted-salt precipitate unquestionably raises the pH of the solution, and it therefore seemed doubtful to us whether the resulting product actually belonged to the heteropoly compounds of the saturated series.

On studying the properties of guanidine molybdates, V. I. Spitsyn and M. P. Rubel found (6) that the normal molybdate is readily soluble in water, while the paramolybdate, $10\ CN_3H_5\cdot12MoO_3\cdot8H_2O$, which forms in the pH range 6.2 to 4.5, has a much lower solubility (about 1 g per 100 ml of solution at 20°). Both compounds crystallize well. In more acid solution (pH about 2) guanidine metamolybdate $2CN_3H_5\cdot4MoO_3\cdot1,5H_2O$, forms, this being apparently an amorphous substance, still less soluble in water (0.38 g per 100 ml of solution at 20°). However, examination under a polarizing microscope showed that its small particles may have the likes of spherolytic structure. The solubility of guanidine paramolybdate and metamolybdate drops considerably in the presence of an excess of the precipitant, i.e., the guanidine salt.

In 1959, V. I. Spitsyn and M. P. Rubel carefully reproduced the conditions of preparation of hepta-substituted guanidine phosphomolybdate, described by A. Rosenheim and J. Pinsker and came to the following conclusion. A tri-substituted yellow salt, $(CN_3H_6)_3[PMo_{12}O_{40}]\cdot 0{,}5\ H_2O$ forms at pH - 2.2 (Fig. 1). This compound contains less water than would be required by the Miolati-Rosenheim theory for the formula $(CN_3H_6)_3H_4[P(Mo_2O_7)_6]$. The addition of 3 gram-equivalents of guanidine carbonate per mole of the tri-substituted salt at 95 to 100° causes the yellow precipitate to dissolve slowly. However, simultaneously there begins to separate a white, slightly greenish precipitate which does not contain phosphorus and is close in composition to guanidine metamolybdate. The pH of the filtrate is 3.1. After

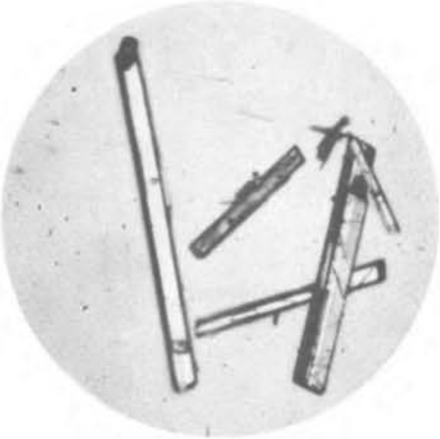

Fig. 1 - Tri-substituted guanidine phosphomolybdate, $(CN_3H_6)_3[PMo_{12}O_{40}]\cdot 0{,}5\ H_2O$. Magnified 150x.

cooling and standing small green crystals fall out. Repeated analyses have shown that the P:Mo ratio in this substance is 1:11, and that it is, therefore, not a derivative of the saturated series. Its composition corresponds to the gross formula $6CN_3H_5 \cdot 1/2\ P_2O_5 \cdot\ 11MoO_3 \cdot 9H_2O$ ("the salt 1:11"). Its crystal form (Fig. 2) and crystallo-optical properties differ from those of the tri-substituted salt. Possibly, it is a double compound of guanidine phosphomolybdate of the unsaturated series and guanidine molybdate, similar to that obtained by V. I. Spitsyn and E. A. Fabrikova as a hydrolysis product of sodium tungstate (see below).

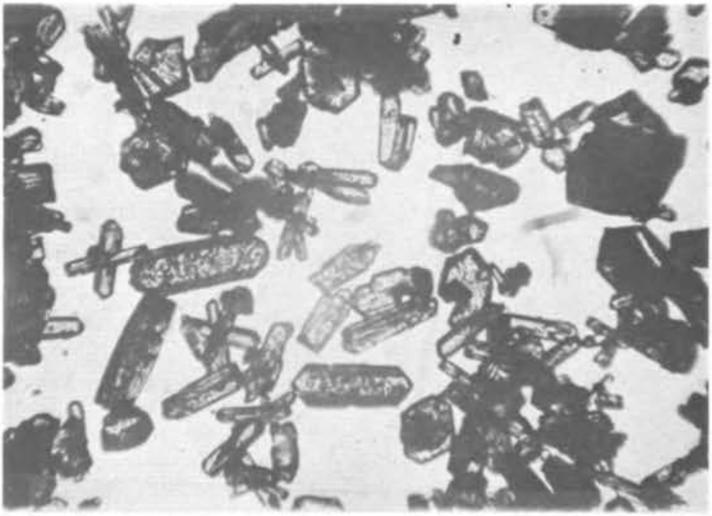

Fig. 2 - The salt $6CN_3H_5 \cdot 1/2P_2O_5 \cdot 11MoO_3 \cdot 9H_2O$, the hydrolysis product of tri-substituted guanidine phosphomolybdate. Magnified 150x.

Addition of 4 gram-equivalents of guanidine carbonate per mole of the tri-substituted salt under the same conditions gave a solution with a pH of 3.9. The white precipitate which appeared in the course of the reaction contained lustrous crystals which dissolved when washed with hot water on the filter. The insoluble residue corresponded to guanidine metamolybdate. The crystals mixed with it turned out to be guanidine paramolybdate. After standing, the green solution threw down crystals of a composition 1:11.

Thus, the addition of guanidine carbonate to a precipitate of tri-substituted guanidine phosphomolybdate raises the pH of the solution from 2.2 to 3.1-3.9, and thus decomposes the initial compound, forming an unsaturated phosphomolybdate, (the most probably luteo-salts, P:Mo=1:9), guanidine metamolybdate and guanidine paramolybdate. The reaction apparently passes as follows:

$$4[PMo_{12}O_{40}]^{3-} + 6\ OH^- \longrightarrow 4[PMo_9O_{31}]^{3-} + 3\ Mo_4O_{13}{}^{2-} + 3\ H_2O \quad (1)$$

$$3\ Mo_4O_{13}{}^{2-} + 4\ OH^- \longrightarrow Mo_{12}O_{41}{}^{10-} + 2\ H_2O \quad (2)$$

$$Mo_{12}O_{41}{}^{10-} + 14\ OH^- \longrightarrow 12\ MoO_4{}^{2-} + 7\ H_2O \quad (3)$$

The required amount of guanidine was about 3-4 g-equivalents per 1 mol of tri-substituted salt and the reactions (1) and (2) and partially (3) could take place. Therefore the salt 1:11 could be represented as a product of interaction between luteophosphomolybdate and molybdate-ions originated from paramolybdate (7):

$$[PMo_9O_{31}]^{3-} + HMoO_4{}^- + MoO_4{}^{2-} \longrightarrow [PMo_{11}O_{39}H]^{6-}$$

Examination of the salt 1:11 with the polarizing microscope, as well as by the immersion method showed it to be a homogeneous substance without appreciable admixture of foreign phases.

If the reaction between guanidine carbonate and tri-substituted guanidine phosphomolybdate is carried out in the same molecular proportions, but at a temperature of 75 to 80° and in more dilute solutions, the molybdic acid will split out of the heteropoly anion more slowly. After cooling and standing, a mixture of a pale green precipitate with small and large green crystals precipitates from the solution. Analysis of such a mechanical mixture gave results close to the composition of the salt described by A. Rosenheim and I. Pinsker, viz.: $7{,}3CN_3H_5 \cdot 1/2P_2O_5 \cdot 12MoO_3 \cdot 9H_2O$. However, elutriation showed this product to be heterogeneous. Besides, if it is examined under a polarizing microscope, crystals of the salt $6CN_3H_5 \cdot 1/2P_2O_5 \cdot 11MoO_3 \cdot 7{,}5\text{-}9{,}5H_2O$ can easily be distinguished, as well as an admixture of amorphous guanidine metamolybdate (Fig. 3).

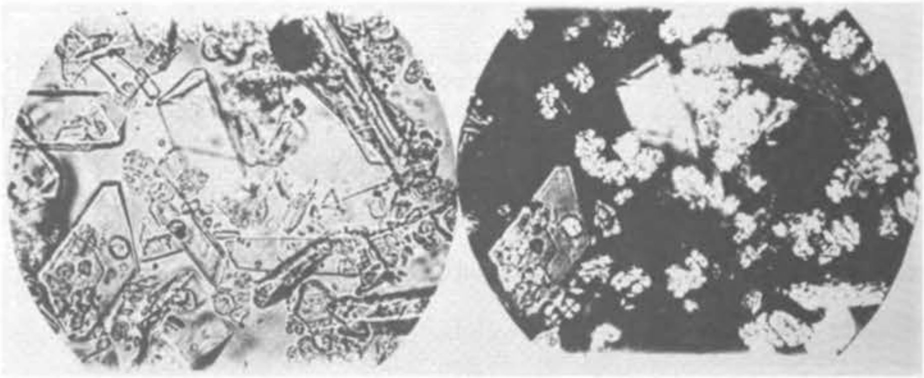

Fig. 3 - "Hepta-substituted" guanidine phosphomolybdate, a mechanical mixture of the salt $6CN_3H_5 \cdot 1/2P_2O_5 \cdot 11MoO_3 \cdot 9H_2O$ and amorphous guanidine metamolybdate.
1--in polarized light; 2--in polarized light with crossed nicols. Magnified 150x.

The results described above lead us to believe that the literature data concerning the existence of high-substitution guanidine salts of phosphomolybdic acid are incorrect.

E. A. Nikitina (8,9) suggested a different method of preparing high-substituted soluble salts of certain heteropoly acids, involving careful addition of an alkali in portions of 1 gram-equivalent per mole of the ordinary-substitution salt. As a result of such fractionated neutralization she described tetra-, penta-, hexa-, and hepta-substituted sodium phosphotungstates, multi-substituted sodium phosphomolybdates and potassium silicotungstates, and a number of other compounds.

There is some doubt as to the individuality of these substances because even undeca-substituted salts were obtained as products of the reaction between phosphomolybdates and NaOH, this being already beyond the Miolati-Rosenheim conceptions. Besides, the addition of the alkali causes the pH of the solutions to rise, which in this case also renders possible partial decomposition of the heteropoly anions.

These assumptions were verified by the radioactive tracer method. V. I. Spitsyn and Yu. I. Bykovskaya (10) have shown that if the solution is acid enough, the central atoms of various heteropoly anions, being quite stable under such conditions, will enter into isotope exchange neither with other heteropoly compounds, nor with ions of the corresponding non-metallic acids. The detection of such an exchange would be evidence of incipient decomposition of the heteropoly anion.

V. I. Spitsyn and E. A. Fabrikova (11) studied, by this means, the interaction between a di-substituted sodium phosphotungstate of the saturated series, $Na_2H[PW_{12}O_{40}]\cdot 14H_2O$, and successively added amounts of NaOH. In one of the runs the anion of phosphomolybdate and in another sodium phosphate present in the solution were labelled with P^{32}. Decomposition of the sodium phosphotungstate by NaOH, accompanied by the splitting-off of phosphate and normal tungstate, was established by two methods (Table 1). In the first method the reaction product was precipitated by quinoline acetate. Free phosphate remained in the solution. With the aid of labelled phosphotungstate the process of decomposition could be observed by the increase of activity in the filtrate or by its decrease in the precipitate. The other method was based on the fact, discovered by the authors, that no isotopic phosphorus exchange occurs between sodium phosphotungstate and phosphate. Labelled phosphate, Na_2HPO_4, of known specific activity was added to alkalized solutions of stable sodium phosphotungstate. On decomposing, the heteropoly compound releases phosphate ions into the solution, which mix with the labelled phosphate ions. And when the heteropoly anion is caused to re-form by adding hydrochloric acid and heating, it now captures labelled phosphorus. The degree of decomposition that took place was calculated from the decrease in the specific activity of the phosphate added, after separating the salts in acid solution by precipitating potassium phosphotungstate. Agreement of the results obtained by the two methods shows that the decomposition of sodium phosphotungstate into sodium phosphate and tungstate begins at pH of 5 after the addition of 5 moles of NaOH per mole of the di-substituted salt. Complete decomposition of the heteropoly anion is accomplished after 25 moles of alkali per mole of phosphotungstate have been added.

Table 1

Decomposition of Sodium Phosphotungstate into Sodium Phosphate and Tungstate in Solutions Containing Various Additions of Sodium Hydroxide

Added NaOH, moles per 1 mole of salt	Atomic ratio Na:P	pH of Solution	Percentage of phosphorus split off from phosphotungstate	
			Method 1	Method 2
0	2:1	2.4	0	0
1	3:1	2.9	0	0
4	6:1	5.0	0	0
5	7:1	6.2	6.0	0
7	9:1	7.2	24.0	20.0
10	12:1	7.5	39.1	35.0
20	22:1	8.2	68.2	70.5
25	27:1	9.0	95.1	98.6

In accordance with these data, chemical analysis of the products formed by the action of 1 mole of NaOH on 1 mole of tri-substituted sodium phosphotungstate, $Na_3[PW_{12}O_{40}]\cdot 15H_2O$ showed that in this case a double salt of the composition $Na_3[PW_9O_{31}]\cdot 3Na_2WO_4\cdot 21H_2O$ is formed. A similar compound was obtained by the direct interaction of sodium luteophosphotungstate with the normal tungstate. X-ray phase analysis demonstrated the individuality of this substance and the difference of its structure from the salt of the saturated series. Thus, even if added in small amounts, alkali will cause partial decomposition of the phosphotungstate anion of the saturated series, making it pass into an unsaturated-series compound, but will not give salts of higher substitution.

Spitsyn and Rubel (1959) studied in an analogous way the interaction between tri-substituted sodium phosphomolybdate and potassium hydroxide. 2 Mols of sodium hydroxide were added to 1 mol of $Na_3[PW_{12}O_{40}]\cdot 26H_2O$. The obtained solution was evaporated at 60° under vacuum and subjected to fractional crystallization.

After standing for several days in a vacuum desiccator above concentrated H_2SO_4, yellow crystals were precipitated and separated from mother liquor. Chemical examination and x-ray analysis showed that the separated fraction consisted of tri-substituted salt, which did not enter into reaction.

The next fraction of crystals obtained under subsequent evaporation of the solution was found to be a mixture of tri-substituted sodium phosphomolybdate and sodium luteo-phosphomolybdate.

The third fraction was nearly pure sodium luteo-molybdate $Na_3[PMo_9O_{31}]\cdot 15H_2O$. It was proved by means of chemical analysis and X-ray examination. The immersion analysis showed that this fraction was a homogeneous phase with its own characteristic refractive index (n_g=1,801 n_p= 1,742).

Examination of the fourth fraction under a polarizing microscope showed that it consisted of two phases. The crystals of luteo-salt constituted the principal of them, meanwhile the other phase was present but in small amount. According to the global analysis proportion P:Mo for the whole fraction was equal to 1:10, i.e. exceeded that corresponding to luteo-salt (1:9). Hence one can conclude that as admixed phase there was molybdate and then most probably, taking in account its range of pH, sodium metamolybdate.

The mother liquor has been left in a vacuum desiccator till its complete evaporation was accomplished. Thereafter the solid product obtained was treated with acetone, which as it is known, dissolves the heteropolycompounds. The solution was evaporated at room temperature. The isolated dry residue according to the chemical analysis and x-ray examination was found to be the tri-substituted phosphomolybdate of saturated series.

The proportion P:Mo equal to 1:35 characterized the part insoluble in acetone. The high content of molybdenum depends doubtless on the presence of sodium metamolybdate admixture because the aqueous solution of this product under the action of guanidine nitrate gives a precipitate, in which the spherolytes of guanidine metamolybdate are detected.

Thus the above suggested scheme of phosphomolybdate-anion hydrolysis under action of guanidine carbonate is also confirmed by the example of reaction of sodium phosphomolybdate with small amounts of sodium hydroxide. The formation of multisubstituted sodium phosphomolybdates under conditions described by Nikitina must be considered as rejected.

V. I. Spitsyn, I. D. Kolli and I. S. Bashkirova (12) studied in a similar way the isotopic silicon exchange between potassium silicotungstate, $K_4[SiW_{12}O_{40}]\cdot 15H_2O$, and silica gel labelled with the short-lived silicon isotope Si^{31} ($T_{1/2}$ - 2.8 hours). Finely powdered rock crystal was irradiated with neutrons in a uranium reactor for 24 hours. Then the preparation was fused with potassium hydroxide. The resulting silicate was decomposed with hydrochloric acid. The silica gel was made free from impurities by repeated decantation. Weighed portions of labelled silicic acid were boiled for 1 hour with the initial potassium silicotungstate solution, as well as with solutions of the same compound preliminarily treated with small amounts of sodium hydroxide and brought to the equilibrium pH value. Then the solutions were centrifuged, the liquid was acidified and poorly soluble cesium silicotungstate was precipitated. If the heteropoly anion decomposed partly when the pH of the solution was raised, the radioactive silicon would incorporate itself in it due to isotopic exchange and would remain fixed in the anion when the solution was acidified again. Thus, the nature of the interaction between the initial salt and the added alkali could be judged by the activity of the cesium silicotungstate precipitate. The results are presented in Table 2.

Table 2

Isotopic Silicon Exchange between Silica Gel and Potassium Silicotungstate Solutions under Various pH Conditions

Added KOH, moles per mole of potassium silicotungstate	pH of solution	Silicon from silicotungstate anion involved in isotopic exchange, per cent
-	4	0
2	5.5	3
6	7.2	8
12	8.1	20

It may be concluded that the potassium silicotungstate of the saturated series does not exchange silicon atoms with a silicic acid precipitate. However, such an exchange becomes detectable when 2 moles of alkali are added per 1 silicotungstate molecule, showing that the silicotungstate anion is beginning to split up. This is just the pH region (5-6) where E. A. Nikitina (8) assumed high-substitution salts to form. It would be more correct to assume that either unsaturated heteropoly compounds of the silicodecatungstate type, or their double salts with the normal tungstates are formed here. Considerable decomposition of potassium silicotungstate is observed at pH - 8, when it evidently passes into the silicoheptatungstate. It should be pointed out that experiments with radioactive indicators show silicotungstates to be much more stable against alkalis than phosphotungstates.

The formation of unsaturated salts on the addition of small quantities of KOH to a solution of potassium silicotungstate of the saturated series has been confirmed by the same authors by direct chemical investigation as well.

Potassium silicotungstate, $K_4[SiW_{12}O_{40}]\cdot 15H_2O$ is not precipitated from solution by acetone. Potassium silicotungstate $K_6[SiW_8O_{29}]\cdot 10{,}5\ H_2O$, obtained at pH of 5.5 to 6.5 by the interaction of potassium silicate with the paratungstate, precipitates from its solutions when acetone is added to them.

On being treated with acetone, the product of the reaction between the tetra-substituted potassium silicotungstate and 2 moles of KOH gave a precipitate which corresponded in composition to the silicodecatungstate. The initial, unhydrolyzed salt was present in the acetone solution. Dissolving of the precipitate and reprecipitation with acetone resulted in the formation of potassium silicooctatungstate. Repetition of this operation caused no further change in the composition of the salt.

It may therefore be concluded that highly substituted potassium silicotungstates do not form in this case too.

The results of our experiments show that the hypothesis of the high basicity of phosphomolybdic, phosphotungstic and silicotungstic acids is not confirmed. It should be considered (7) that the inner sphere addends in heteropoly anions are electrically neutral molecules of the formula H_2RO_4 or RO_3, where R = Mo or W. 4-Coordination should be assumed for the central atom of heteropoly compounds. It is quite possible that the H_2RO_4 molecules link themselves to the PO_4^{2-} or SiO_4^{2-} tetrahedra at the expense of a hydrogen bond. The existence of a tri-substituted guanidine phosphomolybdate with a minimum of bound water shows that in heteropoly anions the central atom and addends of the RO_3 type may also combine with each other through common oxygen atoms.

The maximum basicity of heteropoly acids corresponds to the basicity of the non-metallic acid contained in their structure.

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Study of Chelate Compounds in the USSR (*)

by V. I. Spitsyn and V. V. Zelentsov

Contents

I. INTRODUCTION

Systematic investigations of chelate compounds were initiated in Russia by Tchugaev (1,2) who discovered a sensitive reaction to nickel and palladium with dimethyl glyoxime. Studying dioxime complexes Tshugaev pointed to the role of a grouping that reacts with a number of metals and laid the foundation of the chemistry of cyclic complex compounds by applying to them the laws of organic stereochemistry. He wrote "Not only does the appearance of a cycle during the formation of complex compounds markedly affect their stability, its very character is an essential condition to the formation of a complex unit".

(*) Translated by A. L. Pumpiansky, Moscow

Numerous Soviet scientists have further dealt with chelate compounds being primarily concerned with analytical chemistry. Thus, Kuznetsov has discovered new organic reagents for a number of cations and developed the theory of organic reagent effect (3-10), the Ukrainian chemists headed by Babko (11-13), Peshkova and her coworkers (14-18) as well other chemists (19,20) have been working on the stability constants and products. Of great importance are also the fundamental and experimental works of Sirkyin (21), Dyatkina (21,22), M. A. Poray-Koshits (22,23), Kulberg (24,25), Voznessensky (26), Korenman (27-35), Alimarin (36-44), Yatsimirsky (45,46), and others (47-55).

Systematic investigations of chelate compounds are being carried out by Terentyev (65-67, 148-150), Grinberg (56-58), and Spitsyn (68,72,73,75) and their coworkers.

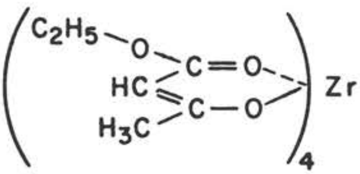
In the present review it is not intended to give an exhaustive survey of investigations carried out in the Soviet Union on chelate compounds but only to show some principal lines along which Soviet scientists have been working during the recent years.

II. SYNTHESIS OF NEW CHELATE COMPOUNDS

1. Complexes with β-diketones

Grinberg and Samoilova (56) have obtained and investigated the properties of palladium acetylacetonate. Its definite molecular weight in benzene amounts to 305 thus substantiating the formula $Pd(C_5H_7O_2)_2$.

Grinberg and Chapursky (57) have studied the synthesis conditions for A. Werner's bivalent platinum acetylacetonates and provided a physicochemical substantiation of the composition of these compounds as shown by Werner's formulas. Thus formula $\mathrm{K}\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\ \mathrm{Pt\ Ac}\right]$ accounts for the orange salt, $\mathrm{K}\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{Ac}\end{matrix}\ \mathrm{Pt\ Ac}\right]$ for the yellow one, and $\left[\mathrm{Pt\ Ac_2}\right]$ corresponds to a canary salt insoluble in water. Cryoscopically determined the molecular weight of platinum diacetylacetonate proves the formula to be correct. The dipole moment of the latter salt in carbon tetrachloride is 1.38 D. The above authors in collaboration with Troitskaya (58) have also obtained and investigated some properties of uranyl acetyl and benzoyl acetonate with the dipole moments being correspondingly 5.12 D and 3.12 D (in benzene). Of great interest is the work carried out by Nesmeyanov and his coworkers on exchange reactions in chelate compounds (59-61) that resulted in the synthesis of formerly unavailable compounds. Thus, for example, the reaction of zirconium tetraacetylacetonate and benzoylacetone produced for the first time zirconium benzoylacetone. Similarly it became possible to synthesise zirconium tetrasalycilaldehyde. It proved to be a solid, sparingly soluble in organic solvents and forming a complex with a chloroform molecule, $(OC_6H_4CHO)_4Zr{\cdot}CHCl_3$. Treatment of tetraacetylacetonate with acetoacetate gave rise to a compound of the following composition



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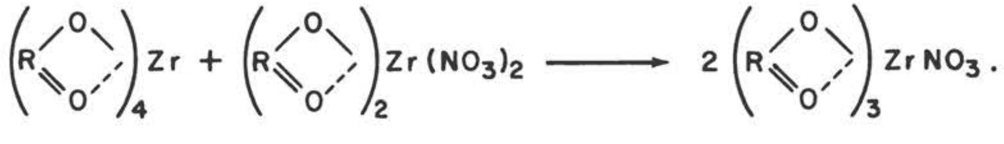
That is a viscous liquid, distillable in vacuo. Similarly, starting from iron triacetylacetonate it proved possible to synthesise iron tribenzoylacetonate and trisalicylaldehyde. The authors showed that the reaction of zirconyl nitrate with acetyl and benzoyl acetone leads to zirconium dinitratediacetylacetonate and dinitratedibenzoylacetonate. The reaction being carried out in the presence of sodium bicarbonate one obtains, correspondingly, nitrates of triacetylacetonate Zr, $(C_5H_7O_2)_3ZrNO_3$, and of tribenzoylacetonate Zr, $(C_{10}H_9O_2)_3ZrNO_3$.

It is of interest that to chelate compounds one can apply the reaction opposite to that of disproportionation, namely



It is for the first time that such a reaction has been applied to chelate compounds.

Other authors have also investigated complex Be compounds with β-diketones (62).

2. Complexes of o-oxyaldehydes and their azomethine derivatives.

Kumov and coworkers have found 2-oxy-1-napthoic aldehyde in alcoholic-alkaline media to form chelate compounds with many bivalent metals of the following composition: $(C_{11}H_7O_2)_2Me$ or $(C_{11}H_7O_2)_2Me \cdot xH_2O$, with Me= Cu^{2+}, Mg^{2+}, Be^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Pd^{2+} (63). These workers have also worked out procedures to evaluate semimicroquantities of various metals with 2-oxy-1-naphtoic aldehyde (64).

Of interest is the work of Terentyev dealing with chelate compounds of copper, cobalt, and nickel with Schiff's bases of salycilic and 2-oxy-1-naphtoic aldehydes (65-67, 148-150). Spitsyn, Zelentsov, Savitch, Pikaev, et al. (68-77), succeeded in synthesising a great number of coordination compounds of uranyl and demonstrating the coordination number of uranium (VI) to depend on the nature of Schiff's base (70-72). The authors were the first to synthesise chelate compounds of molybdenyl with Schiff's bases of the said aldehydes and of some aromatic amines (73,74) by making Schiff's base react with molybdenyl chloride in ether solution. Similar compounds of copper, nickel, and vanadium have also been obtained and investigated (75-77).

Schiff's bases such as salicylal-o-aminophenol proved useful in the luminescent analysis of metals (78).

3. Complexes of 8-oxyquinoline, its derivatives, and 8-mercaptoquinoline

There is no need to deal in detail with numerous works concerning the production of chelate compounds of 8-oxyquinoline and its 5,7-dihaloid derivatives.

One must, however, mention the study of chelate compounds of some bivalent cations and 8-oxyquinoline derivatives such as the Mannich bases (79-81). This work carried out by Spitsyn, Trailina, Zelentsov and Savich is to some extent the continuation of investigations previously undertaken by Phillips. The above authors synthesised several new Mannich bases and obtained on their basis chelate compounds of molybdenum (VI). tungsten (VI),uranyl, cobalt (II), nickel (II), and copper (II).

The study of absorption spectra in ultraviolet and visible regions showed the spectra of starting organic compounds to be almost similar to those of chelate compounds obtained therefrom, this having enabled the authors to estimate the molecular weight of the latter compounds spectrophotometrically (80).

One is especially to note the work carried out in the Latvian S.S.R. by Bankovsky et al., who suggested a simplified procedure to obtain 8-mercaptoquinoline and its derivatives (82-84). The investigation of the properties of thiooxine and those of its chelate compounds with a number of metals permitted the authors to recommend the use of thiooxine and its derivatives as new analytical reagents (85-98).

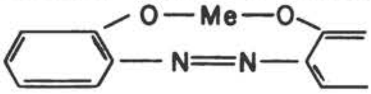
4. Chelate compounds with complexones

A number of scientific bodies of the USSR such as the All Union Reagent Research Institute, the Biochemical Institute of the Medical Academy, the M. V. Lomonosov Moscow State University are concerned with producing new complexones.

Lastovsky, et al., are extensively investigating the possibilities to synthesise new complexones and to use them in analytical chemistry (99-101). Thus, for example, they have studied the coordination properties of hexamethylenediaminotetraacetic and phenyliminodiacetic acid. The stability constants of a number of cations with these complexones were investigated polarographically. Spitsyn, et al. (102,103), as well as other authors (104-110) have been undertaking systematic studies of complexes of rare elements with complexones and the applicability of complexones to separation of these elements.

5. Complexes with azo compounds and other organic substances

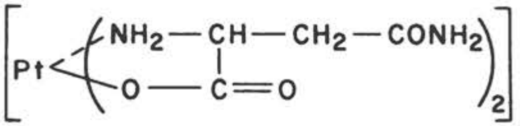
A whole series of chelates obtained by the interaction of cations with azo compounds, of the general formula:



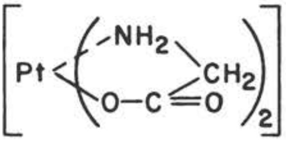
has been investigated (111-113).

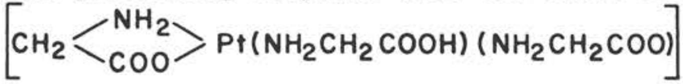
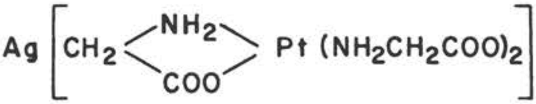
Stepanov found that the formation of copper chelates with azo compounds markedly affects the reactivity of the latter (114,115).

Vainstein (116) obtained a co-ordination compound of bivalent platinum with asparagine:

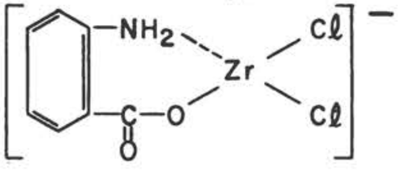


and showed that the non-cyclic salt of diglycinodiglycine platinum can be converted to a chelate salt

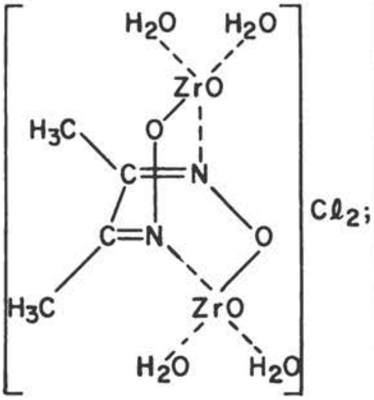
cis 

the conversion proceeding stepwise with the first step being the acid  $\left[CH_2\begin{matrix}NH_2\\COO\end{matrix}Pt(NH_2CH_2COOH)(NH_2CH_2COO)\right]$ isolated as silver salt  $Ag\left[CH_2\begin{matrix}NH_2\\COO\end{matrix}Pt(NH_2CH_2COO)_2\right]$ (117).

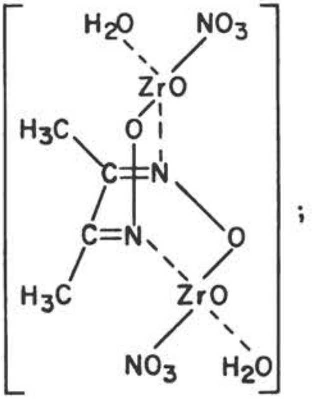
A compound was obtained (118) that proved to be zirconyldichloroantranylic acid whose anion corresponded to the formula:



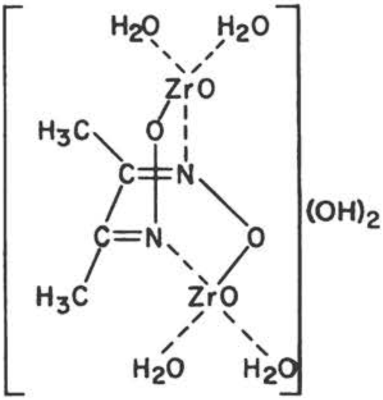
Zirconyl, ZrO^{2+}, glyoximes, were demonstrated to have the following structural formulas (118):



glyoximine zirconyl-chloride

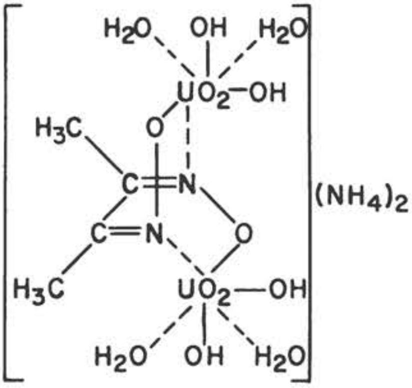


glyoximine zirconyl nitrate



glyoximine zirconyl hydroxide

The inner sphere of zirconyl glyoximines is thus characterised by the presence of three six membered rings, in two of which is involved each ZrO^{2+} ion and a dimethylglyoxime molecule and the third ring binds two zirconyl ions with two NO groups. The authors succeeded in obtaining a complex of dimethylglyoxime and uranyl to which they assigned the formula



They suggested that the probability of obtaining complexes of hydrolisible elements with nitrogen containing addenda would depend on the possibility of cyclic bond formation.

It would be possible to go on enumerating the synthetic works on chelate compounds. It seems, however, worthwhile to consider in more detail some fundamental problems concerning the structure of these compounds and the character of the bond Me- ligand.

III. STRUCTURE OF CHELATES AND CHEMICAL BONDING

Along with numerous synthetic investigations a number of laboratories in the Soviet Union are extensively studying the structure of chelates bearing in mind their intermediate position between organic chemistry and chemistry of co-ordination compounds.

The greatest attention is thereby devoted to the problem of π -interaction between metal and ligand.

Calvin and Wilson had suggested that in the molecules of acetylacetonates are formed multiple bonds Me-O involving unshared pairs of d-electrons of the Me-atom and $p\pi$ electrons of the oxygen atom of the acetylacetone cycle (119).

X-ray structural investigations begun in the early fifties by Shugam et al., led to definite conclusions about the character of the bond in these compounds. It was shown that the structure of acetylacetonates Cu (II), Al, Cr (III), and Co (III) displays some interesting regularities, the most important of them being the non-valent character of the metal atom bond with oxygen atoms of acetylacetone molecule, the equivalence of these bonds, and the delocalisation of conjugated double bonds in the six membered ring.

When investigating the acetylacetonates of aluminum, chromium and cobalt the above authors bore in mind that these compounds differ in the structure of their d-orbitals: the aluminum atom has less tendency to form co-ordinating compounds than chromium, cobalt and copper atoms because it has no d-electrons.

Table 1

Values of interatomic distances and valent angles in molecules of aluminium (I), chromium (II), and cobalt (III) acetylacetonates.

(Following Shugam and Shkolnikova (123)).

	I	II	III
Me-O	1.95 ± 0.02Å	1.90 ± 0.03Å	1.90 ± 0.03Å
C - C	1.38 ± 0.04Å	1.40 ± 0.04Å	1.41 ± 0.04Å
C - O	1.28 ± 0.02Å	1.28 ± 0.04Å	1.27 ± 0.04Å
$C-CH_3$	1.58 ± 0.03Å	1.53 ± 0.04Å	1.54 ± 0.04Å
Valent angle			
O-Me-O	89° ± 1°	93° ± 1°	90° ± 1°
Me-O-C	131° ± 2°	131° ± 3°	132° ± 3°
C-C-C	127° ± 3°	127° ± 3°	130° ± 3°
O-C-C	122° ± 4°	118° ± 4°	118° ± 4°

It will be seen from the Table that in the acetylacetonates in question the metal atom forms six equivalent covalent bonds. The double bonds C=C and C=O in the acetylacetone cycle are delocalised. The above data allowed the authors to suggest that the character of the bond Me-O and the delocalisation of double bonds is not dependent on the state of electrons on the d-orbits of metal atoms. In the acetylacetonate molecules of transition metals either bearing on d-orbits unshared electron pairs or not, and in the aluminium acetylacetonate molecule with no d-electrons in the atom, the double bonds are found delocalised independent of the nature of the metal atom. The interatomic distances Me-O in aluminium, chromium, and cobalt acetylacetonates being rather similar, the authors postulated that there takes place no formation of multiple bond Me-O involving unshared pairs of d-electrons of the Me atom or $\rho\pi$ electrons of the oxygen atom. The formation of bonds Me-O that introduce into the system of conjugated bonds C=O and C=C, on delocalisation of double bonds, a third, additional, multiple bond and give thereby rise to a 'benzoid' structure in the acetylacetone ring appears to be due to the possibility of making use in the general system of π-interaction in the metal ring of ρ-orbits of the metal atom (129).

The conclusion about d-electrons of the metal atom not participating in the even bond Me-O is substantiated by the theory of crystalline field. The acetylacetone group $C_5H_7O_2^-$ does not create any strong crystalline field and, hence, is not capable of markedly affecting the energetic state of d-electrons that is, leads to their compulsory sharing. This is also accounted for by the data on magnetic moments of acetylacetonates and cyanide complexes of some transition metals.

The conclusion about the delocalisation of double bonds taking place whether there are unshared electron pairs in the metal atom or not, and even with d-electrons absent was also derived from the study of infra-red spectra that proved to be almost identical (130,131).

Later Shigorin, et al., demonstrated that in such molecules as acetylacetonates with π-electrons the group Li-O, Al-O, etc., are involved in the formation of even bonds. In these compounds the energy of secondary element-metallic bonds is determined in terms of the equation $E= E_d + E_a + E_\pi$, where E_d and E_a is the energy of dipole and acceptor-donor equilibrium. The member E_π determines the interaction energy of the group Me-O with π-electrons of the system and has the highest value. In systems such as acetylacetonates six electrons of the system (four π-electrons of C=C and C=O and two of the primary bond Me-O) gives rise to quasiaromatic cycles with π-electron interaction.

The main factors determining the formation of a ring with π-electron interaction and equivalent bonds are as follows. Firstly, the deformation of the electron cloud of the group Me-O in a direction perpendicular to the bond $\sigma \longrightarrow \pi$ favoured by strong σ-π conjugation Me-O-C=C. Secondly, availability of free ρ - or d-orbits at metal atoms to be used by π-electrons of the double bonds (C=O, etc.). Thereby, the π-electrons of C=O groups make use of the free orbit of the atom (Li, Al, etc.) to form a peculiar molecular three centered orbital, this also accounting for the redistribution of π-electron density in the system.

The investigation of the structure of nickel diethyldithiocarbonate (126) enabled to demonstrate that Ni is situated in the centre and has a flat square configuration. The valent angle of SNiS is 82°. The deformation of valent angles in nickel diethyldithiocarbamate cycle is of the same order as in five and six membered cycles.

It is of interest to note that the authors came to the conclusion that the comparatively rarely encountered four membered cycles in chelate compounds are due to the instability of organic substances involving two functional groups at a carbon atom rather than to their low stability owing to high deformation due to the deformation of valent angles.

The distances C-S and C-N, amounting to 1.62 Å and 1.26 Å, correspondingly, are markedly shortened as compared to the single bonds, pointing to a strong interaction between sulphur and nitrogen atoms, that is thought by the authors to be strongly influenced by the unshared pair of electrons of the nitrogen atom and the free d-orbits of sulphur atoms. This interaction hinders the formation of a dative metal atom bond with sulphur atom as proved by the Ni-S distance being equal to 2.27 Å. Simultaneously, the donor-acceptor bond Ni-S, by withdrawing electrons from the sulphur atom favours the interaction of sulphur and nitrogen atoms. This interaction turns thereby to be the strongest in the chelate compound.

It has been also shown that nickelsalicyloximate crystallises to yield two modifications often isolated from the same solution (128). For one of these modifications the molecule of the complex has been shown to be flat. The C-C- distance in the benzene ring remains constant. The distances Ni-O and Ni-N amount to 1.83 Å and 1.86 Å, correspondingly, i.e. to the sum of their covalent radii. The valent angle at Ni is 96°. That the bond lengths of metal-ligand are equalised points to the delocalisation of π-electrons.

Copper and lead diethyldithiocarbamates (127,134) as well as zinc 8-mercaptoquinolinate (127) were also under investigation. Though nickel and copper diethyldithiocarbamates involve the same space group ($p2_1/c$) they are not isomorphous, the nickel atoms occupying a particular and the copper atoms the general position.

Zinc mercaptoquinolate $(C_9H_6SN)_2Zn$, is to be referred to the space group lbm2, that has no symmetrical centre as substantiated by the presence of piezo electric effect. Lead - diethyldithiocarbamate isolated as monoclinic crystals has two modifications. X-ray study of the first modification (parameters: a=9.55; b=11.75; c=14.72; z=4) showed the lead atom as situated at the apex of a tetrahedral pyramid with four sulphur atoms in its base. The interatomic distance is 2.7 - 2.8 Å, that coincides, within the precision of estimation, with the sum of covalent radii.

In their review X-ray structural investigations of chelate compounds (132,133), Shugam and Shkolnikova pointed out that the six membered cycles are characterised by complete delocalisation of conjugated bonds, the conjugation in the five membered cycle not being as complete and clear cut.

This allowed the authors to conclude that there is no delocalisation of bonds in the five membered cycle of metal dimethylglyoximates. There is also a difference in the character of deformation of valent angles of six and five membered cycles.

The fact that in no case where one could suppose π-bond formation has any noticeable decrease in the distance Me-O, that with acetylacetonates is near to the sum of covalent radii, been found, does not invalidate the arguments in favour of $d\pi - \rho\pi$-interaction in chelate compounds, nothing being known to what extent the interatomic distances can be decreased due to $d\pi - \rho\pi$-interaction, but it shows that this interaction does not result in the interatomic distance decreasing by more than 0.02-0.03 Å. The formation of multiple bonds Me-O is possibly due to the p-orbits of the metal atom being involved in the general system of π-interaction.

Recently Bokiy (135) proposed to consider compounds characterised by one or several multiple bonds between the central atom and ligands as a separate group of complex compounds. This group could also involve chelate compounds. This follows from the consideration that if the bonds involve a different number of electrons then the types of bonds must also necessarily be different. The author speaks in particular about such complex compounds with multiple bonds whereas addends are used single oxygen or nitrogen atoms, say, the chelate compounds UO^{2+} and UO_2^{2+} As the 'uranyl diagonal' is only 10% shorter than other ligand bonds situated at the vertexes of somewhat or strongly distorted cube, U has a coordination number of 8 and its structure is that of a coordination polyhedron that is a distorted cube or in the limit a hexagonal pyramid.

The presence in the complex of multiple bonds makes other bonds much ionic. Therefore, the number of such ligands will not always be strictly constant for a particular central atom. The uranyl group is often surrounded by four, five, or six addenda (136). The same suggestion was also made by Zelentsov and Savich (70-72) for uranyl chelate compounds with Schiff bases. It has been shown that depending on the character of Schiff base the uranium coordination number may be 6, 7, and 8, because in uranyl salicylalethylenediiminate and complexes with similar Schiff bases that are tetradentate ligands, the coordination number of the central atom is six and the structure is that of a square bipyramid. The addition of a molecule of polar solvent such as alcohol or pyridine leads to the uranium coordination number increasing to seven and the structure of such complex compounds corresponds to that of a pentagonal bipyramid. The coordination character of the bond is revealed by the fact, that it proved possible to eliminate the added molecule only after prolonged heating at 160-180°. This is also substantiated by the marked change in the colour of the chelate. No more than one solvent molecule is usually added this being probably due to considerable distortions of valent angles of Schiff's base molecule. It is not the case with complexes of uranyl and such Schiff bases as salicylalaniline. Our complexes of uranyl and 2-oxy-1-naphtal-4-iodoaniline and 4-methyl-salicylal-4-iodoaniline contained, as shown by elemental analysis, two pyridine molecules that could not be eliminated even on heating for a long time at 160-180°. The temperature being raised up to 200-220° the complexes were destroyed. It seems that here pyridine is coordinated. With tridentate ligands such as 2-salicylalaminopyridine and its derivatives very stable chelates were formed (68,72). The coordination number was thereby 8. The structure of uranium compounds having a coordination number 8 seems to correspond to a hexagonal bipyramid. To this type, according to Bokly, must also be referred vanadyl chelates with Schiff bases, having the structure of a square pyramid, distorted along the coordinate V-O, with d^2sp^2 – bonds (75).

As to the chelate structure, Bokiy and Poray-Koshitz (171) point out that they may be somewhat different from those of common coordination compounds because the formation of metal rings affects to some extent the chemical bond between the metal and ligand. It is therefore not to be excluded that with bi- and tridentate addenda the tetrahedral coordination in paramagnetic nickel complexes (just as the flat one in diamagnetic complexes) will prove to be more common than in the presence of simple monodentates. We proved it actually to be the case by studying the magnetic susceptibility of nickel chelates with several Schiff bases (77). The structure of nickel complexes depends on the character of the radical of the azomethine group added to nitrogen. The nature of the radical markedly affects the redistribution of electron density ultimately determining the bond type and the stereochemistry of the complex.

If the Schiff base nitrogen is bound with hydrogen atoms or aliphatic radical, these compounds are diamagnetic and hence flat. But if as a radical bound with the nitrogen of the azomethine group is used a system with π-electrons (such as phenyl), then the complexes are paramagnetic with magnetic moments $\sim 3.00\ \mu\zeta$. We have suggested these nickel complexes be tetrahedral. In contrast to 2-oxy-1-naphtal-4-iodoanilate nickel ($\mu_{\text{eff.}}=3.04\,\mu\zeta$) its dipyridine derivative, being octahedral, has a smaller magnetic moment ($\mu_{\text{eff.}}=2.90\,\mu\zeta$).

Our data substantiate the suggestion (137) that the orbital magnetism must be exhibited in octahedral complexes with free spins such as d_{ϵ}^{1} (Ti^{3+}), d_{ϵ}^{2} (V^{3+}), $d_{\epsilon}^{4}d_{\gamma}^{2}$ (Fe^{2+}), $d_{\epsilon}^{5}d_{\gamma}^{2}$ (Co^{2+}), but not in the case of d_{ϵ}^{3}(Cr^{3+}), $d_{\epsilon}^{3}d_{\gamma}^{1}$ (Cr^{2+}), $d_{\epsilon}^{6}d_{\gamma}^{2}$ (Ni^{2+}) and $d_{\epsilon}^{6}d_{\gamma}^{3}$ (Cu^{2+}).

If there is no sharing of electrons, octahedral complexes in nickel compounds must as a rule have smaller magnetic moments than the tetrahedral ones. Thus, with octahedral bond distribution, the electron configuration of Ni (II) complex corresponds to $d_{\epsilon}^{6}d_{\gamma}^{2}$, and that of a tetrahedral complex $d_{\epsilon}^{4}d_{\gamma}^{4}$. It will be seen that in the external magnetic field the electron density d_{ϵ}^{6} remains constant whilst d_{ϵ}^{4} changes thus causing orbital magnetism to rise. These considerations are in accord with the above experimental data. Magnetochemical investigations find an ever increasing recognition as an important procedure in the study of chelate structure.

On the basis of magnetic susceptibility of coordination compounds 1,3,5-triphenyl-,=1-p-tolyl-3,5-diphenyl-1-p-chlorophenyl-3,5-diphenyl, and 1,0-carboxyphenyl-3,5-diphenyl formasanes Co^{2+}, Ni^{2+} and Cu^{2+}, the authors (138,139) consider their structure to be flat.

The study of the dipole moments of acetylacetonates of Zr, Th, In, Be, Al, Cd, Cu, and their oxyquinolates unexpectedly did not reveal any electric symmetry either in solutions or in a solid state (140). On the ground of their experimental as well as literature data the authors conclude that acetylacetonates and oxyquinolinates of the said metals have some constant electric moment that seems to be accounted for by not completely symmetrical space structure.

Table 2

The dipole moments of acetylacetonates in solution (140)

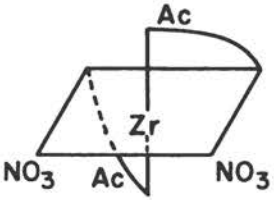
Compound	Solvent	P_2	P_e (R)	μ, D
$(C_5H_7O_2)_2Be$	CCl_4	85.22	58.85	0.71
-"-	C_6H_6	87.70	59.22	0.79
-"-	$C_4H_8O_2$	88.06	59.04	0.80
$(C_5H_7O_2)_3Al$	CCl_4	128.59	90.00	1.03
-"-	C_6H_6	130.52	89.24	1.08
-"-	$C_4H_8O_2$	130.07	88.51	1.11
$(C_5H_7O_2)_4Zr$	CCl_4	157.50	128.00	1.45
-"-	C_6H_6	197.30	128.54	1.46
-"-	$C_4H_8O_2$	201.03	128.43	1.52
$(C_5H_7O_2)_4Th$	CCl_4	202.21	127.40	1.58
-"-	C_6H_6	203.60	126.91	1.60
-"-	CH_8O_2	201.78	127.12	1.57
$(C_9H_6NO)_4Zr$	$C_4H_8O_2$	279.77	189.98	1.97

Table 3

Electric properties of acetylacetonates and oxyquinolates in solid state (140)

Compounds	P_d	$P_e(R)$	P_a
$(C_5H_7O_2)_2Cu$	68.80	65.05	3.75
$(C_5H_7O_2)_2Be$	74.62	59.22	15.40
$(C_5H_7O_2)_2Cd$	67.41	55.03	12.38
$(C_5H_7O_2)_3Al$	106.40	89.25	17.15
$(C_5H_7O_2)_3In$	96.10	88.00	8.10
$(C_5H_7O_2)_3Cr$	108.23	95.15	13.08
$(C_5H_7O_2)_4Zr$	152.70	128.50	24.20
$(C_5H_7O_2)_4Th$	150.24	127.14	23.10
$(C_9H_6NO)_2Cu$	102.43	96.07	6.36
$(C_9H_6NO)_2Cd$	95.50	89.65	5.85
$(C_9H_6NO)_3In$	152.74	145.36	7.38
$(C_9H_6NO)_3Al$	154.60	144.00	10.60
$(C_9H_6NO)_4Zr$	198.85	189.00	9.85
$(C_9H_6NO)_4Th$	205.90	190.85	15.05

It will be seen from Table 2, that μ is independent of the solvent. Thus a great difference between the molar (P_2) and electric polarisation (P_e) cannot be accounted for by the solvent effect. The data in Table 3 show that the magnitude deformation polarisation P_d amounting for the solid state to the sum of electron and atom polarisation is almost the same as that of electron polarisation (refraction). This allowed the above authors to conclude that the difference $P_2 - P_e$ is not wholly due to atom polarisation and, hence, the compounds studied have no abnormally high atom polarisation that formerly was supposed by many workers to be the reason for the appearance of a rather considerable dipole moment. The authors found the zirconium dinitrodiacetylacetonate molecule (60) to have a moment 7.94 D. in benzene and 7.76 D. in dioxan, this pointing to cis-form:



with Ac being acetylacetone.

The application of the magnetic resonance phenomena allowed to work out a new method of investigating chelate formation in solutions (141-147). When forming a complex the coordinating particles screen the paramagnetic ions from the water molecule protons. This increases the mean distance of the possible approach between paramagnetic ions and protons that, in turn, leads to the weakening of their dipole magnetic interaction and, hence, to the increase in the time of relaxation T_1 (T_1 is the 'lateral' time of nuclear relaxation, or the transfer of energy following the exponential law e^{-t/T_1} . The difference in crowding of energetic sublevels depends on the rate with which protons supply to the environment the energy taken up from the radio frequency field). Evaluating the relaxation time of solvent protons it is thus possible to obtain information on the extent to which the central atom of the complex is screened by ligands and on the size of particles formed. The above method permitted the determination, for example, of the composition and stability constants of antipyrine complexes of trivalent iron as well as to show that the monoethanolamine and triethanolamine complexes of Mn (II), and monoethanolamine complex of Ni (II) are coordination compounds.

Using paramagnetic resonance it proved possible to show (115) copper chelates to have a much narrower band on introduction of substituents partaking in π-electron interaction. In co-ordination derivatives of copper and azo compounds the magnitude of ΔH becomes still smaller. This points to the effective interaction of the unshared electron of copper atom with π-electrons of the azo group and through the latter with π-electrons of the entire system. This interaction seems to affect markedly the ion interaction of electrons of copper atoms resulting in the narrowing of the absorption band. The authors believe that the introduction of substituents into the molecule would lead to the change in the crystalline lattice, affecting both the ion interaction and the inner crystalline field that exerts an influence either on the form or the width of bands owing to the anisotropy of the g-factor. The sharp narrowing of bands in passing from copper acetylacetonate to its derivatives cannot be accounted for by ion interaction that should in this case decrease.

Investigating the paramagnetic spectra of solutions the authors found, that while the spectra of acetylacetonate and its derivatives are similar to the spectra of these substances in solid state, the spectra of azo compounds reveal only bands of superfine scission, pointing to the interaction of copper atom electron with nitrogen nuclei of the azo groups. This led the authors to conclude that the unshared copper electron of coordination compounds interacts with π-electrons of the system, its contribution depending on the nature and structure of the surrounding groups. The infrared study of some chelates suggested (148-150) that the number of infrared bands in the range of N-H valent vibrations (3000-3500 cm.$^{-1}$) allows to distinguish between the flat, trans-configuration and the cis, or tetrahedral configuration. It has been shown that with trans-forms symmetric vibrations occur with no change in the dipole moment and infrared spectra, whilst for cis- and tetrahedral forms both symmetric and antisymmetric vibrations are found to be active. The authors studied the infrared spectra of salicylaliminates of Cu, Ni, Pb, Be, and Cd, acetylacetonyliminates of Cu, Ni, and Pd, N-oxyacetophenoiminate of Cu, 2-oxy-1-naphtaliminates of Cu and Ni, as well as copper salts of ethylene-bis-α-iminopropionic and ethylenebis- -phenylacetic acids. Only for salicylaliminates of Cu and Ni, acetylacetonate iminates of Cu and Pd, and 2-oxy-1-naphtyliminates of Cu and Ni does one observe an intensive absorption band corresponding to antisymmetric N-H vibrations. The authors believe the presence of this band to prove these complexes to be trans.

There are two bands observed for salicylaliminates of Be and Cd corresponding to symmetric and antisymmetric N-H valent vibrations. The distance between these bands is 100 cm^{-1}, in accordance with tetrahedral structure of these complexes. The spectra of copper salts of ethylene-bis-α-iminopropionic and ethylene-bis-α-phenyl acetic acid also reveal two absorption bands.

The definite conclusion made by the authors is that the presence in the spectra of chelates containing the N-H group, of only one group in the range of valent vibrations of N-H constitutes a proof of the complex being flat and trans. A number of workers have dealt with the dependence of coordination compounds of a number of metals in ultra-violet and visible regions on the ligand structure (151-159).

IV. CHELATE POLYMERS

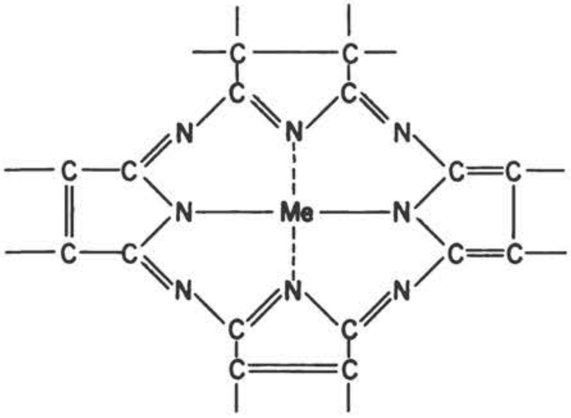
It is of interest to mention the work carried out to produce new types of chelate polymers and study their physicochemical properties. As early as 1946 Berlin (160) observed that polymers and copolymers of acrylic acid yield thermostable, not melting and insoluble coordination compounds with bi- and polyvalent metal ions. Berlin suggested to use this reaction to produce thermostable polymeric plastics.

Korshak, et al., are concerned with obtaining new chelate polymers (161-164). As starting compounds for chelates are used such newly synthesised substances as bis-β-diketones, bis-(8-oxyquinoline)-methane and other compounds that can give rise to polymers.

It has been shown that thermal stability of polycoordination compounds starting from bis-β-diketones involving phenyl molecules depends on the quality of the latter. Thus, the high thermal stability is displayed by derivatives of terephtalyldiacetophenone (three phenyl groups separated by three carbon atoms) and the least by derivatives of adipyldiacetophenone (two phenyl groups separated by ten carbon atoms).

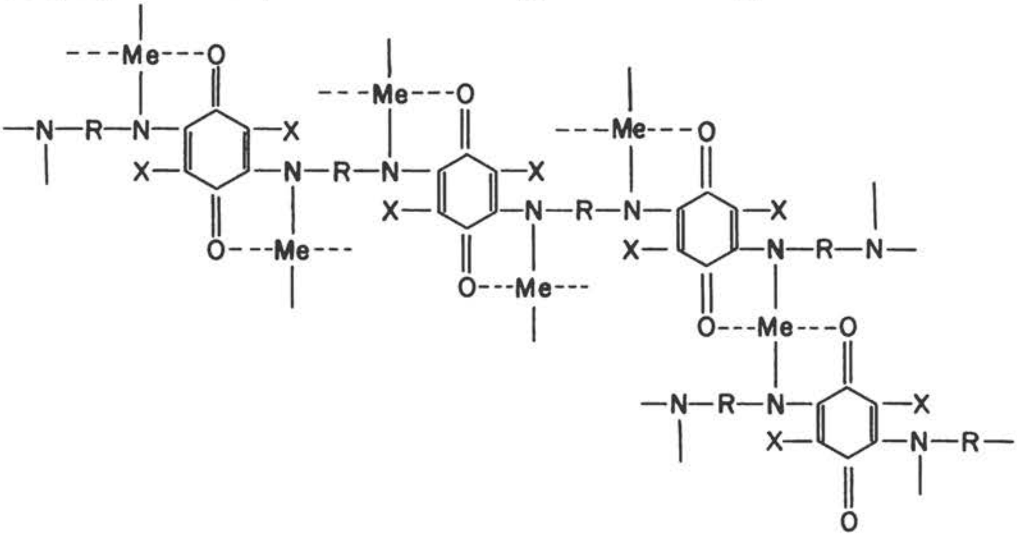
The investigation of properties of polymers obtained by the interaction of Be, Mg, Ca, Zn, Cd, Ba, Fe (II), Co (II), Ni (II), Cu (II), and Al with 1,4-xylene(bis-(acetylacetone)) showed that the most stable compounds are the derivatives of Be and Ba and the least stable ones those of Zn and Ca (165).

Berlin, Matveeva, and Sharle (165) have obtained a new type of polymeric chelates composed essentially of carbon, nitrogen and metals. These polymers were prepared starting with tetracyanoethylene and bivalent cations. The reaction of one mole of copper acetylacetonate and two moles of tetracyanoethylene in vacuo at 160 to 300° gives rise to a coordination reaction accompanied by evolution of acetylacetone. The polymer formed is a non-melting black substance insoluble and not decomposing in organic solvents, alkali or diluted acids. Its infra-red spectrum did not reveal any intensive absorption bands over the 700 to 3000 cm.$^{-1}$ range but for the 2224 cm^{-1} band, corresponding to the CN group. The authors explain the absence of absorption bands in the above region as due to the formation of polymeric structure of the postulated composition



The polymer samples show broad bands of electron paramagnetic resonance of high intensity with the distance between the maxima of 500 to 700 oersted. Heating for six hours of this polymer at 500° leads to its magnetic susceptibility rising from 10×10^{-6} to 50×10^{-6} with the copper percentage in the heated and starting polymer remaining almost the same (170). The reaction of an equimolecular mixture of copper acetylacetotetracyanoethylene and phthalonitrile results in the formation of a copolymeric chelate of a linear structure (168).

Berlin and Matveeva (167-169) have prepared polymeric chelates starting with polyaminoquinones they were first to synthesise. The reaction of polybenzydenedichloroquinone, obtained on condensation of equimolecular amounts of chloranyl and benzydene in the presence of sodium acetate, with copper, iron, cadmium, magnesium, and other salts gives rise to polymeric compounds containing from 6 to 15% metal:



Polyaminoquinone, that by itself is paramagnetic, becomes considerably more sensitive when structured with copper (166). The authors think that this increase in sensibility cannot be entirely accounted for by the introduction into the polymer of copper for a similar effect can be produced by conventional thermal structuring without introducing metal. Thus copper seems to play an additional role, that of ordering the structure.

V. CONCLUSION

The last decade was characterised by an ever increasing interest in the chemistry of chelates both from the practical and fundamental point of view. Science cannot develop without constant exchange of views. An extensive use of all results already achieved necessary for further development, is an essential condition for the progress in science. The present review dealing with the work of Soviet scientists on coordination compounds is to be considered as a contribution to the exchange of ideas between scientists of our countries.

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