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FIFTY YEARS OF SOVIET PHYSICAL CHEMISTRY

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The Soviet period in the development of physical chemistry in our country is characterised by an extremely rapid increase in the volume of scientific research and in the number of specialised scientific topics investigated.

The appearance of the physicochemical laboratory underwent a radical change. The Soviet generation of physical chemists has witnessed on more than one occasion an almost complete technical re-equipment of its laboratories, brought about by the impact of modern experimental methods borrowed from physics, electronics, and computer science. The interface between physical, organic, inorganic, and analytical chemistry is now almost completely blurred. Physicochemical methods and concepts have become predominant in the study and interpretation of the results obtained in fundamental studies of every aspect of chemical science.

The rapid and fruitful penetration of the theoretical and experimental methods of modern physics concerns practically every problem in physical chemistry (structure of matter, valence theory, chemical equilibria, kinetics and mechanism of chemical change, problems in photochemistry and radiation chemistry, electrochemistry, semiconductor chemistry, theory of heterogeneous catalysis, chemistry of surface phenomena, colloidal chemistry). In the last fifty years, important advances have been made in all these fields, and many of the most important fundamental ideas of chemistry have had to be revised. The close association of organic and inorganic chemistry with physical chemistry (the "chemification" of physical chemistry) has given rise on the one hand to the appearance of new and rapidly developing branches of science such as physical organic chemistry, and on the other hand to the far-reaching penetration of mathematics into the whole of theoretical and applied chemistry. This tendency has become even more marked as a result of the increasing use of modern computing techniques.

Significant advances in the principles and methods of industrial chemistry have been both the result and the motivation of the development of physical chemistry. New methods of carrying out chemical reactions were quickly introduced into the chemical industry: these include the separation and purification of liquids and gases, sorption techniques, new and versatile continuous catalytic processes, and definite progress towards the rational control of chemical reactions including the development of chemical cybernetics. The physical chemistry of surface phenomena, electrochemistry, and radiation chemistry are helping to solve important technical problems, such as the development of new methods of preparation of disperse materials, the conversion of chemical into electrical energy, and problems in radiation-chemical synthesis. The growth of physical chemistry has been of tremendous importance also in the polymer field. The present review will not deal specifically with this field, which has become a self-contained branch of modern chemistry.

If we compare the development of Soviet chemistry with that of the rest of the world we see that our Soviet science leads (or keeps pace with) the science and technology of advanced capitalist countries in many important branches of chemistry. These include chemical kinetics, the theory of catalysis, electrochemical kinetics, adsorption theory, physicochemical mechanics, combustion and explosion problems, and many others.

These important advances in physical chemistry cannot be understood otherwise than in the context of earlier developments in this science. It is well known that physical chemistry first arose in our country at about the time when chemistry began to claim the status of a science in its own right. Lomonosov was the first to propose the term "physical chemistry" for the branch of science which straddles the boundary between chemistry and physics, and gave the following definition of this scientific discipline: "physical chemistry is a science which explains in terms of the concepts and experiments of physics that which takes place in mixed bodies during chemical operations"[1]. Lomonosov also carried out the earliest experimental physicochemical investigations in the chemical laboratory of the Academy of Sciences, now inseparably associated with his name.

Nearly all the main sections of physical chemistry began gradually to take shape during the second half of the nineteenth century. The first ideas on catalysis were put forward, studies of chemical affinity began, progress was made in the study of electrochemical phenomena, heat effects accompanying chemical change were investigated, the universal gas law was established, the simplest laws of chemical kinetics were formulated, and above all the fundamental laws of thermodynamics were determined.

Physical chemistry experienced a particularly significant development during the period immediately preceding that discussed in the present review (from the 1880's to the 1920's). Much was accomplished during this period, particularly development in chemical thermodynamics.

During the nineteenth and especially the early twentieth centuries some higher scientific institutions in St. Petersburg, Moscow, Kazan', Kiev, Khar'kov, Yur'ev, and other cities had better laboratories than those of the Academy, and therefore the role of the Academy of Sciences in the development of chemistry (and in particular physical chemistry) was not so much to strengthen experimental research within its own walls as to stimulate the scientific life of the nation by electing leading scientists as Members, by sponsoring prizes, and by publishing scientific work[2].

After the Great October Socialist Revolution, following Lenin's instructions, the Academy of Sciences began a systematic study and survey of the natural industrial resources of Russia, and set up the first Chemical Institutes. At the same time, various subsidiary research institutes were founded, and some of these have played a major role in the development of Soviet physical chemistry[3,4].

At present, the most important physicochemical institutes of the Academy of Sciences are the Institute of Chemical Physics, the Institute of Physical Chemistry, and the Institute of Electrochemistry.

In May 1958 the Central Committee of the Communist Party of the Soviet Union issued important directives for the faster development of chemical industry and science. Since then, the Academy of Sciences has created and successfully developed a number of new physicochemical institutes. These include the Institute of Electrochemistry

of the Urals' branch, which specialises in the electrochemistry of fused salts and solid electrolytes, and also the Institutes of Catalysis and of Chemical Kinetics and Combustion of the Siberian Section of the Academy of Sciences of the USSR.

Many other institutes of the Academy have some involvement in physicochemical investigations: the Institute of Organoelemental Compounds, the Zelinskii Institute of Organic Chemistry, the Kurnakov Institute of General and Inorganic Chemistry, the Institute of High-Molecular-Weight Compounds, the Institute of Petrochemical Synthesis, etc.

Physicochemical studies at one of the oldest of the chemical institutes of the Academy of Sciences—the Radium Institute—also produced notable contributions. In 1961 this Institute was transferred from the Academy of Sciences to a different administration.

Foremost among the other physicochemical institutes are the Karpov Physicochemical Institute, the Pisarzhevskii Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, and the Faculty of Chemistry of Moscow State University.

The origin and the earliest development of chemical physics took place at the Leningrad Physico-Technical and Radiographic Institute (GFTRI) under the direction of A. F. Ioffe. In 1921, a small team led by N. N. Semenov was set up within the GFTRI to study electronic effects in chemistry[5]. This laboratory investigated electric fields, molecular physics, and electronic phenomena. Towards the beginning of 1931 the activities of the electron chemistry laboratory had progressed well beyond the scope of a section of a research institute. At about this time the whole of the scientific world had began to associate research in chemical physics with the name of Semenov and his coworkers. As a result of the phenomenal growth of the Leningrad Institute, the decision was made in September 1931 to reorganise it into a physico-technical scientific research complex, consisting of three independent research institutes. One of these institutes, opened on the 15th October 1931, was the Leningrad Research Institute for Chemical Physics. Since that day, having achieved independent status, the Institute of Chemical Physics (IKhF) has intensified its efforts towards its basic objective: to introduce the theories and methods of physics into chemistry, the chemical industry, and many other branches of the national economy.

The scientists of the Institute have gone a long way from the first researches, made thirty-five years ago, to the modern work in the most varied aspects of chemical physics. In 1939 the Institute was admitted into the Academy of Sciences of the USSR.

The branch of the Institute created in 1957 and staffed almost exclusively by young scientists is beginning to produce good results. The Institute is still directed by its founder, Nobel Laureate and Hero of Socialist Labour N. N. Semenov.

The Institute is now investigating the kinetics and mechanism of chemical reactions (chain reactions in particular), and the kinetics and mechanism of catalytic processes, chemical processes induced by penetrating radiations, at low and at high temperatures, under high pressures, etc. It is developing new processes and improving existing processes for the production of polymers and monomers, it is studying the degradation and stabilisation of polymers, it is developing new physical methods and apparatus for chemical investigations such as mass spectrometry, radiation spectrometry, the Mössbauer effect, etc. It is refining the theory of combustion and detonation processes in gaseous and condensed systems, studying the kinetics of biological processes, and applying physicochemical investigations to the mode of action of chemicals and of physical agents on various biological systems.

In 1967 the Institute of Chemical Physics was awarded the Order of Lenin for its achievements in the development of chemical physics and the training of specialists.

Another important centre of physical chemistry in the Academy of Sciences of the USSR is the Institute of Physical Chemistry. The history of this Institute goes back to 1930, when the Laboratory for Colloid Chemistry and Electrochemistry (LAKE) was set up at the initiative of V. A. Kistyakovskii[6]. In this laboratory, he and his pupils studied problems of metal corrosion, electrocrystallisation [electrodeposition], and flotation.

When the Academy of Sciences moved to Moscow in 1934 the Praesidium of the Academy reorganised the Laboratory into an Institute for Colloid Chemistry and Electrochemistry (KEIN), with a more comprehensive research programme. In addition to the above topics, the Institute undertook problems in colloid chemistry, the physicochemical dispersion of metals, the theory of lubrication, the formation of metallic coatings, and several others.

V. A. Kistyakovskii was the director of these establishments until 1939, when he was succeeded by A. N. Frumkin, whose main activities had previously been centred at the Karpov Physicochemical Institute and Moscow State University.

In 1945 the Institute of Physical Chemistry (IFKh) was created from the Institute for Colloid and Electrochemistry.

From 1949 until 1953 the Institute of Physical Chemistry was directed by G. V. Akimov. During this period the Corrosion Section, led by Akimov, grew rapidly.

At the moment the following topics are being pursued at the Institute: the physicochemical mechanics of metals, concrete, and colloidal systems; the forces acting close to phase boundaries and in thin films; the formation and precipitation of aerosols; the thermodynamics and kinetics of sorption on carbon and mineral sorbents, and chromatography; the protection of metals against corrosion; the preparation of polymer coatings. Problems in radiochemistry and radiation chemistry also claim a significant part of the effort of the Institute.

Since 1953 V. I. Spitsyn has been the director of the Institute as well as leader of the work on radiochemistry.

In 1958 the Institute of Electrochemistry (IELAN), based on the Electrochemistry Section of the Institute of Physical Chemistry, was created on the initiative of A. N. Frumkin in response to the need for more extensive work on electrochemical kinetics (the theoretical basis of the most important practical applications of electrochemistry).

In the 1950's some problems of major importance to the national economy and demanding an increased effort in the field of electrochemical kinetics began to be clearly recognised. These include the realisation of electrochemical power sources (fuel cells) able to convert the chemical energy of a fuel directly and continuously into electrical energy; the development of electrochemical transducers

for automation, control, and guidance systems having a number of valuable properties, especially the ability to operate at low frequencies; the provision of methods of electro-synthesis of organic compounds offering very pure products; and various other problems.

Investigations are now proceeding at the Institute in the following directions: the theory of electrochemical processes and the structure of the metal/electrolyte interface; the electrochemistry of organic compounds; the mechanism of processes in electrochemical power sources (particularly fuel cells), in electrochemical transducers, and in the electrochemical machining of metals; surface phenomena on semiconductors (including organic semiconductors); the mechanism of radiation processes; the quantum theory of chemical reactions; physicochemical hydrodynamics and its application to the theory of technological processes.

Since its foundation the Institute has been directed by A.N. Frumkin, Hero of Socialist Labour and president in 1965–66 of the Comité International de Thermodynamique et de Cinétique Électrochimiques (CITCE).

The structure and reactivity of a wide range of organoelemental compounds are being investigated at the Institute of Organoelemental Compounds (INEOS). The Zelinskii Institute of Organic Chemistry (IOKh) is examining spectroscopically the molecules of organic compounds. Nearly half of the work of the Institute is directed towards a study of the catalytic interconversions of hydrocarbons. The Topchiev Institute of Petrochemical Synthesis (INKhS) is developing catalytic methods for converting hydrocarbons into valuable chemicals, and is working on plasma chemistry and on the physical chemistry of polymers. Work on the physical chemistry of the oriented state has reached an advanced stage at the Institute of High-Molecular Compounds (IVS). The Kurnakov Institute of General and Inorganic Chemistry (IONKh) is the principal centre in our country for the development of the field of research originated by Kurnakov: physicochemical analysis. This includes studies of the physicochemical properties of various groups of compounds, metals, salts, semiconductors, organic compounds, and also the conditions of equilibrium in multiphase systems. Extensive investigations are proceeding at the Institute on the structure of complex compounds of a great variety of metals, including the platinum, transuranium, and rare elements. At the Kazan' Institute of Organic and Physical Chemistry (IOFKh) work is directed towards electrochemical methods of metal treatment and the electrocrystallisation [electrodeposition] of metals.

The Karpov Physicochemical Institute was the first (and, until the 1930's, the only) institute in this country with a physicochemical objective. The Institute began operations in 1918 as the Central Laboratory of the Chemistry Section of the Supreme Economic Council (VSNKh). A.N. Bakh[7-9] was one of the founders of the Institute, which he directed continuously for 28 years.

Since those early years, Bakh has gathered together some talented young scientists, and has created, with the support of the Government, an ideally equipped institute whose scientists are continually striving towards linking science with technology.

A.N. Frumkin took an active part in developing the Institute as a physicochemical establishment, and was its Deputy Director from 1929 until 1947, when he was succeeded by V.A. Kargin. The present Director of the Institute is Ya.M. Kolotyrkin.

The leading physicochemical experimentation and the major theoretical advances for which the Institute was responsible have won the acclaim of scientists in the Soviet Union and abroad. During the pre-war period, the activities of the Institute were aimed mainly at three large sections of physical chemistry: surface phenomena and electrode processes, the structure of matter, and chemical kinetics and catalysis. Since the war, there has been a considerable increase in the effort devoted to polymer science and catalysis. Studies in radiation chemistry and in the separation of mixtures have grown into fields of study in their own right. Important problems solved at the Institute include the development of new processes and the improvement of existing processes for chemical technology.

The Karpov Institute has also undertaken a heavy load of organisational work to assist the development of Soviet physical chemistry. It has convened regular series of conferences and published physicochemical journals. The Institute still retains close links with the Academy of Sciences. Many dozens of scientists now working in our country have been trained at the Institute.

The Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR[10] was founded a few years after the Karpov Institute (in 1927), but it has also won a leading place among the Soviet institutes specialising in physical chemistry.

Much of the work of this Institute is devoted to studies, by ESR, infrared spectroscopy, and other methods, of the structure, reactivity, and transformations of free radicals formed during electrochemical reduction, and of the sterically stabilised radicals which act as oxidation inhibitors in polymers. Other activities include the mass-spectrometric and isotopic study of various organic reaction mechanisms, of the mechanism of oxidation of various ions by peroxides, of adsorption phenomena, of the mechanism of the radiation-induced and the oxidative degradation of polymers, and an ESR study of the kinetics of fast protolytic reactions.

Extensive developments have taken place in mechanistic and kinetic studies of industrial catalytic processes, and of the part played by macrokinetic factors, in relating catalytic activity to thermodynamic properties, in systematising and correlating data on catalysis with a view to developing a theory for the selection of catalysts.

Furthermore, the Institute is now successfully engaged in the following directions: the utilisation of solar energy, the use of nuclear radiations in chemistry, the synthesis of zeolites, and studies of sorption mechanisms.

Physicochemical investigations at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR have been highly significant: this applies particularly to the work on the thermodynamics and kinetics of complex-formation reactions and on the theory of chemical bonding in complexes (K.B. Yatsimirskii), on comprehensive studies of different problems in the electrochemistry of fused salts (Yu.K. Delimarskii), on colloidal chemistry, and on a number of other problems.

Many important physicochemical projects are being developed in the Academies of other republics of the Soviet Union: the electrodeposition of metals at the Academy of Sciences of the Lithuanian SSR (Yu.Yu. Matulis), heterogeneous catalysis and the theory of acids and bases at the Academy of Sciences of the Kazakh SSR (D.B. Sokol'skii and M.I. Usanovich), polymer mechanics at the Academy of Sciences of the Latvian SSR, the structure of inorganic

compounds at the Academy of Sciences of the Moldavian SSR, etc.

Among the institutions engaged in physicochemical research, a leading place belongs to the Chemistry Faculty of the Lomonosov Moscow State University [11,12]. The history of this faculty goes back to the creation, during the earliest years of Soviet rule (1919–1921), of a chemistry section of the Faculty of Mathematics and Physics, and to the organisation (in 1922) of a Scientific Research Institute for Chemistry within the University. The Chemistry Faculty of Moscow State University achieved independent status in 1929–1930.

In 1929 a Chair in Physical Chemistry was created as part of the Chemistry Faculty. This department grew quickly, and established a number of laboratories. By 1930–1932 it included the following laboratories: electrochemistry (A. N. Frumkin), contact processes for the heavy chemical industry (N. N. Petin), halurgy (A. V. Rakovskii), photochemistry (A. I. Rabinovich), and colloid chemistry (V. A. Naumov). Some of these laboratories eventually grew into independent departments.

When the Chemistry Faculty was organised, the Chair of Physical Chemistry was entrusted to A. V. Rakovskii. After his death (in 1941) it passed to A. V. Frost, and is now held by Ya. I. Gerasimov.

The Department of Physical Chemistry is a large scientific research establishment engaged in wide-ranging investigations into chemical thermodynamics and thermochemistry, catalytic reaction mechanisms, adsorption, molecular spectroscopy, colloid chemistry, the electrochemistry of gases, and electron diffraction studies of molecules. Other sections of the department are investigating the physical chemistry of disperse systems, electrochemical kinetics, the physical chemistry of high polymers, and chemical kinetics. Many of the sections are led by Academicians and Corresponding Members of the Academy of Sciences of the USSR. The Chemistry Faculty of the Zhdanov Leningrad State University is investigating ion-exchange theory (B. P. Nikol'skii), the thermodynamics of multicomponent systems and electrochemical kinetics. Physicochemical research is active also in other institutes of higher education such as the Mendeleev Moscow Institute of Chemical Technology, the Lomonosov Moscow Institute of Fine Chemical Technology, the Odessa State University, the Tomsk State University, etc.

Thus, in contrast to the pre-revolutionary period, physicochemical research is being carried out in large scientific complexes operating by a predetermined plan which reflects modern trends of research as well as the needs of the national economy, and not by individual scientists assisted at the most by a few coworkers.

In conclusion, we note that in recent years the network of physicochemical journals has grown appreciably (but less so than in the advanced capitalist countries). Before the war only two specialist physicochemical journals were published in our country: Zhurnal Fizicheskoi Khimii and Kolloidnyi Zhurnal, as well as the foreign-language publication Acta physicochimica USSR (which ceased to exist in 1946). Now, in addition to these, we have Elektrokhimiya, Khimiya Vysokikh Energii, Zhurnal Strukturnoi Khimii, Kinetika i Kataliz (the last two being published by the Siberian section of the Academy of Sciences of the USSR), and Zashchita Metallov (published jointly by the State Committee for Science and Technology, the Ministry of the Chemical Industry, and the Academy of Sciences).

Having briefly described the growth of the network of scientific establishments specialising in physical chemistry and their role in the overall scientific context, we shall discuss the major results obtained during the past 50 years. Through lack of space, this review must be a fragmentary one, and many important achievements have had to be omitted.

MOLECULAR STRUCTURE. REACTIVITY. QUANTUM CHEMISTRY. PHOTOCHEMISTRY

Soviet scientists are successfully investigating the relationship between the structure and the reactivity of molecules, the theory of elementary chemical processes and of energy-transfer processes, the theory underlying the application of radio-frequency spectroscopy (ESR and NMR) to the study of the structure and properties of matter, chemical spectroscopy, the Mössbauer effect, X-ray and electron diffraction, and the theory of molecular vibrations. In many of these topics important progress has been made in spite of the relatively small number of workers engaged.

Scientists of the Soviet Union have made outstanding contributions to developments in the chemistry of complexes, and to studies of their structural features. The foundations were laid by the work of L. A. Chugaev, who carried out systematic studies of the complexes of platinum metals even before the revolution [13]. Chugaev founded one of the leading schools of research on complexes. The able scientists who joined Chugaev (I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinskii, N. K. Pshenitsyn, O. E. Zvyagintsev, and others) carried on the work of their teacher with outstanding success. They prepared hundreds of previously unknown complexes, studied their properties, and found practical uses for them. Chernyaev put forward the rule of the trans effect—an important generalisation of the influence of inner-sphere substituents in the coordination compounds. The trans effect concept gave a theoretical foundation to the development of multistage methods of preparation of complexes having a prescribed structure and configuration. Studies of the mutual effect of ligands (of which the trans effect is a special example) became the central theme of a great deal of chemical work in the USSR and abroad. The trans effect was demonstrated not only on platinum, but on many other elements: rhodium, cobalt, iridium, rhenium, etc. In ruthenium compounds the cis effect (first discovered by Grinberg) was investigated as well as the trans effect.

Grinberg and his coworkers were among the first to apply radioactive isotopes to the study of the structure and properties of complexes. Specially important results were obtained in their work on the kinetics of exchange between ligands and ions in solution.

Recent structural studies, carried out mainly at the Kurnakov Institute of General and Inorganic Chemistry, have added considerably to our understanding of the shapes (spatial structures) of complex ions of various metals. In particular, it was shown that the less usual polyhedra (coordination numbers five and seven) are fairly common among transition metals, and that frequently the structure is polymeric either due to bridging atoms or groups of atoms (halogens, oxygen, water, or hydrazine molecules, etc.) or due to metal–metal bonds (as in the acetato-complexes of univalent and bivalent rhodium and the halides of bivalent rhenium). These structural studies, together with the results of other physicochemical investigations, have identified and characterised some new types of chemical

bond (many-centre bonds in transition metal compounds, partial bonds, and particularly metal–metal bonds). Much valuable information on the structure of inorganic compounds was obtained in studies of the infrared spectra of coordination compounds.

The research on quantum chemistry led by Ya. K. Syrkin and M. E. Dyatkina deserves a special place among these investigations.

Syrkin was among the first in the USSR to undertake work on quantum chemistry and has developed it successfully up to the present time. His quantum chemical calculations of the energy and other properties of organic and inorganic compounds have led to many important predictions. He successively developed the theory of covalent bonds in inorganic compounds and the concept of covalent bonding in crystals which has proved so valuable in understanding the properties of semiconductors.

Much of Syrkin's effort was devoted to problems in the physics of the elementary chemical act. He put forward the original view that the elementary acts of many chemical reactions occur through five-, six-, or seven-membered rings with a sextet of electrons.

In recent years he has actively investigated the mechanism of reactions involving aromatic metal complexes (ferrocene, ruthenocene, etc..) and the π-complexes of some platinum group metals.

Dyatkina made a significant contribution to the theory of inorganic chemistry. She published many papers on the theory of directional valencies and the theory of the valency states of atoms in molecules. These include the most systematic investigation of the valency states of both transition and non-transition elements, from which many conclusions of the greatest importance in inorganic chemistry may be drawn.

Syrkin and Dyatkina developed the most satisfactory of the existing theories of aromatic and π-complexes of metals, and made a systematic study of the electronic structure of the tetrahedral oxo-anions of the transition metals.

A fundamental contribution to the application of the X-ray structural method to problems in inorganic chemistry, resulting in the development of crystal chemistry, came from N. V. Belov and his students (Institute of Crystallography of the Academy of Sciences of the USSR). They identified the structural units in silicates, explained the function of the cations, and computed a large number of complicated silicate crystal structures.

Since 1944, the Institute of Organoelemental Compounds led by A. I Kitaigorodskii has studied the packing of organic molecules in crystals. The concept of close packing of molecules, the principle of identifying the structure on that basis (the so-called "geometrical analysis"), and the symmetry rules following from the basic packing law—all these were rapidly adopted both in the field of low-molecular compounds and in the high polymer field. The laboratory developed improved physical methods for the structural investigation of organic and organoelemental compounds, originated and developed a new branch of crystal chemistry (organic crystal chemistry), proposed a method of quantitative conformational analysis, and is now successfully engaged on developing the basic aspects of the physics of organic crystals.

The same laboratory is carrying out wide-ranging investigations of the reactivity of organic and particularly of organoelemental molecules.

An extensive series of investigations by D. N. Kursanov on the chemistry of the carbonium ion, the mechanism of dehydration of alcohols, and the reactions of quaternary ammonium ions has shown that these processes involve a carbonium mechanism.

Other work by Kursanov on heterolytic reactions has dealt with hydride transition reactions. This work has made significant contributions to modern views on the hydride mobility of hydrogen in organic compounds.

The classical work of Kursanov on the reactivity of non-benzenoid aromatic systems is widely known.

Organometallic compounds have made possible a clear demonstration of dual reactivity in the absence of tautomerism. On this basis, M. I. Kabachnik drew a distinction between the phenomena of dual reactivity and tautomerism as equilibrium isomerism. He subsequently developed a quantitative theory of tautomeric equilibrium as an acid–base equilibrium, and discovered new experimental approaches to the study of these phenomena.

The work of R. Kh. Freidlina in new areas of organic chemistry has become widely known: it includes radical telomerisation and the regrouping of radicals in solution, as well as methods of synthesis based on these phenomena.

The simultaneous discovery by the Soviet physicists L. I. Mandel'shtam and G. S. Landsberg and by the Indian physicist Raman of the molecular light-scattering method was of incalculable importance in developing the science of the structure of matter. Thie method was widely used by B. A Kazanskii at the Institute of Organic Chemistry in studies on hydrocarbons.

A systematic investigation of the spectra of compounds having different combinations of atomic groups, by P. P. Shorygin of the Institute of Organic Chemistry, allowed him to establish the main rules which relate the spectra of molecules to the specific parameters of the chemical bonds and of the system of energy levels in a molecule. From these studies it has been possible to characterise the effect of substituents on π-bond systems as a function of the position of the substituent atom in the Periodic Table, of the type of intermediate units, of the orientation in space of the interacting groups, and of the chain length of the conjugated structural elements. A specific effect of heavy atoms contacting π-bond systems through an intermediate atom (oxygen, methylene, or other groups) has been discovered and investigated.

The work of A. N. Terenin[14] on the photodissociation of molecules has played a fundamental role. This worker was the first to put forward a correct model of the mechanism of the primary interaction of a quantum of light with a molecule. Terenin's work provided the foundations of the electronic theory of the structure and energetics of molecules. The classical papers by Terenin on the photochemistry of halide vapours are of fundamental importance to the basic problem of photochemistry—the mechanism of the primary elementary process. These investigations are attracting renewed interest in connection with the problem of a quantum light source.

Studies of compounds in the gas phase led to the discovery of various new phenomena: the "activation" of the fluorescence of complex molecules by adding other gases, and the effect of light gases (helium and hydrogen) on the intensity of absorption by complex gas molecules.

One of Terenin's students, B. S. Neporent, made an important contribution to the spectroscopy of complex mole-

cules: he proposed a rational physical classification based on intramolecular interactions of the various types of state (electronic and vibrational).

A series of papers by Neporent was devoted to spectral studies of intermolecular interactions in condensed media. He found a solution of the complicated problem of the influence of the solvent on the intensity of molecular spectra: this provided the foundations for the development of general methods of absorption spectral analysis.

M. V. Vol'kenshtein (Institute of High-Molecular Compounds, Academy of Science of the USSR) made a number of theoretical investigations of intensities in the infrared and Raman spectra of polyatomic molecules, of problems in rotational isomerism, and in the field of molecular optics. Some of Vol'kenshtein's work dealt with problems in quantum chemistry.

An important series of investigations into quantum chemistry was carried out recently in Sokolov's laboratory of the Institute of Chemical Physics. A quantum-mechanical model of the hydrogen bond was developed, an effective method was found for optimising approximate wave functions and the operators used to calculate various characteristics of atoms and molecules, and a simple and effective method was proposed for calculating the magnetic screening constants of nuclei in NMR spectra.

The study of elementary processes in gases led to the development of a theory of the thermal decomposition of molecules which takes account of the non-equilibrium nature of the process. Problems arising in the application of resonance spectroscopy in chemistry were investigated, and a useful method was developed for calculating the transition probabilities of spin–lattice relaxation for paramagnetic ions and radicals in solids.

Wide-ranging investigations of the structure and reactivity of molecules are in progress at the Moscow State University.

O. A. Reutov's team is working on a number of theoretical problems in organic chemistry, with special reference to organometallic compounds, and is using many physicochemical research techniques: the stereochemistry and kinetics of substitution reactions at a saturated carbon atom, the mechanism of free-radical reactions in the liquid phase, the mechanism of the synthesis of organometallic compounds, and many others.

The laboratory of V. M. Tatevskii is investigating the detailed relationship between the spectra and the structures of hydrocarbons of various classes, and is looking into some problems in the theory of molecular structure and in the dynamics and statics of molecular systems.

A. I. Shatenshtein (Karpov Institute) made a systematic study of the kinetics and mechanism of hydrogen exchange in non-aqueous solvents (NH_3, HF, etc.). The assumption underlying this work is the acid–base character of hydrogen exchange in solutions, with the postulate that hydrocarbons can take part in protolytic reactions with strong bases and acids.

The X-ray laboratory of this Institute (G. S. Zhdanov) has also made substantial contributions to our knowledge of the structure of matter and to our understanding of the nature of the chemical bond by systematic crystal-chemical studies of important groups of chemical compounds.

CHEMICAL KINETICS. THEORY OF COMBUSTION AND EXPLOSION PROCESSES

During the past few decades it has become clear that chemical reactions as a rule are complicated processes consisting of many elementary acts and proceeding with the participation of various frequently unstable intermediates. It is not surprising, therefore, that the scope of chemical kinetics should have begun to increase even in the 1920's, when workers began to seek out the laws controlling complex reactions, and the general features responsible for the peculiar course of the majority of chemical reactions. The young Soviet physical chemistry took an active part in the creation of the new chemical kinetics, achieving a position of leadership in a number of aspects [15].

The acknowledged centre of this work in the Soviet Union was the Institute of Chemical Physics, with its affiliated establishment. However, the ideas and methods of modern chemical kinetics spread far and wide to other institutes, both academic and affiliated, and also to university laboratories.

The largest contribution to the development of this branch of science came from the school of N. N. Semenov, who created the modern theory of chain reactions by unifying an enormous fund of experimental data. These were exhaustively explained by considering the relationship between the rates of the various processes involved in the mechanism of chain reactions (generation, propagation, branching, and breaking).

The results obtained in 1926 by Semenov's coworkers Yu. B. Khariton and Z. F Val't in their work on the quenching of luminescence in a mixture of phosphorus vapour and oxygen gave additional impetus to the development of the theory of chain reactions. New phenomena were discovered which transcended the scope of existing views on the mechanism of chemical change: these were the strikingly sharp transitions of reactive mixtures from a state of almost complete inertness to a violent reaction, accompanied by ignition.

To explain this phenomena Semenov put forward the concept of branching chain reactions, which quickly gained wide acceptance. If the number of chain-branching events is greater than the number of chain-breaking events, the reaction rate steadily increases due to the continuous appearance of new chains until ignition of the mixture of reactants sets in ("chain explosion"). Semenov proposed the idea of chain breaking at the walls of the reactor. The theory of chain breaking in the volume of the reactor was developed independently by Semenov and Hinshelwood.

Semenov and his coworkers (Yu. N. Ryabinin, A. V. Zagulin, A. A. Koval'skii, and others) discovered in 1928–1930 the existence of sharp explosion limits in the oxidation of sulphur vapour, hydrogen, carbon monoxide, and hydrogen sulphide, thus increasing manyfold the number of known examples of ignition and demonstrating the generality of branching chain reactions.

Besides the chain explosion process, another very important and common type of ignition is known: the so-called thermal explosion. This type of explosion is due to the disruption of thermal equilibrium in the system, leading to a progressive increase in the reaction rate until explosion sets in.

In 1928, Semenov published a quantitative theory of thermal explosion, as well as the theory of chain ignition,

entitled "Theory of Combustion Processes". In that same year A. V. Zagulin confirmed Semenov's formula relating the explosion pressure to temperature for a number of systems (explosion of chlorine dioxide, explosion of hydrogen/chlorine mixtures, etc.), thus demonstrating the correctness of the thermal explosion theory. Semenov's monograph "Chain Reactions", published in 1934 in the Soviet Union and in 1935 in England, was based on the whole of this work. The book treats the massive array of existing experimental data on the kinetics of gas-phase reactions (and some liquid-phase reactions) from the point of view of the theory of chains [16,17].

In the years that followed, research on chemical chain reactions reached enormous proportions both in our country and abroad. Among the workers at the Institute of Chemical Physics, M. B. Neiman and his coworkers produced extensive evidence that the oxidation of hydrocarbons involves a degenerate branching mechanism. Neiman also examined in detail the two-stage ignition of organic compounds; the essential feature is that hydrocarbons, aldehydes, alcohols, etc., often burn in two stages: the cold flame stage and the hot flame stage. Mention must also be made of the work of A. A. Koval'skii and M. V. Polyakov on homogeneous–heterogeneous reactions and of Koval'skii's localised calorimetric method, which enabled him to show that many catalytic reactions begin at the catalyst surface but continue in the gas phase, where they follow a chain mechanism. A. B. Nalbandyan demonstrated that branching chain reactions can be controlled by controlling the rate of heterogeneous chain breaking; with N. M. Emanuel' and others he also investigated homogeneous catalysis in oxidations and many other reactions. The work on the influence of catalytically active additives on the initial stages of chain oxidations in the gas or the liquid phase has revealed new methods of controlling chemical processes under industrial conditions.

More recently, new and useful concepts have appeared in this work, such as the stimulation of slow branching chain oxidations, which make use of the self-accelerating and self-maintaining properties of branching chains.

In joint work by Nalbandyan and members of the Institute for the Chemical Industry, homogeneous catalysis was used to develop a new technological approach to the production of formaldehyde by the oxidation of natural gas.

Chain theory had been formulated on the basis of formal kinetics: it still needed additional chemical foundations. It was essential to establish the nature of the active centres in chain reactions and of the elementary processes which constitute the mechanism of a chain reaction, and to measure the rate constants of these processes. Only by the application of the newer physical methods could these problems be solved. For a number of years, V. N. Kondrat'ev and his coworkers have been developing various methods of this type which allow free atoms and radicals to be studied under the conditions existing during a chemical reaction (the spectroscopic resonance, absorption method, the catalytic recombination method). By these methods it was shown that OH radicals and H atoms are present in the combustion zone of hydrogen, carbon monoxide, and other gases at the appropriate concentrations for flame conditions. These active particles were shown to play an essential role in the development of the reaction. The rate constants of the elementary processes involving OH radicals and H atoms were measured, and in this way a full quantitative description of a branching chain reaction was obtained: the oxidation of hydrogen, a model gas-phase oxidation reaction. A monograph by A. B Nalbandyan and V. V. Voevodskii gives a detailed quantitative analysis of this reaction.

Voevodskii introduced the concept of the role of heterogeneous factors in the theory of the cracking of alkanes. This allowed him to explain a number of difficulties encountered by the generally accepted theory of Rice. As a result of his work on the structure and properties of free radicals, he discovered a new type of free-radical reaction and put forward a quantitative theory of the cracking of alkenes. In his studies of the recombination of atomic hydrogen on catalytically active surfaces, Voevodskii identified two régimes under which this process can take place: a high-temperature and a low-temperature régime; he also measured the recombination efficiency on metallic and oxide catalysts. These results, combined with a number of theoretical generalisations, led to the realisation that heterogeneous–catalytic reactions can occur by a mechanism analogous to the chain mechanism.

V. I. Gol'danskii made a detailed study of the general theory of tunnelling transitions in chemical reaction kinetics assuming both maxwellian and quantum energy distributions of the reacting molecules.

These, and many other investigations on a variety of reactions of different classes of compounds, have produced convincing evidence that, as suggested by Semenov in his book, chain reactions are of common occurrence.

Furthermore, even in 1939–1940 (in the year following the discovery of the fission of atomic nuclei by Hahn and Strassmann), N. N. Semenov's coworkers Yu. B. Khariton and Ya. B. Zel'dovich had published the first essentially correct theory of the uranium fission chain reaction.

The mass spectrograph was used for the first time ever to solve a problem in chemical kinetics in V. N. Kondrat'ev's laboratory. As a result of the work of V. L. Tal'roze, the mass spectrometric method is now widely used to study complex chemical mixtures and processes.

S. Z. Roginskii and his coworkers were among the first (together with A. I. Brodskii of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR) to use labelled atoms in chemical kinetics.

The use of polarography to investigate molecular intermediates in complex chain reactions has thrown light on the mechanism of many oxidations of organic compounds (V. Ya. Shtern and coworkers).

Nowadays, new methods are used to study the mechanism of electronic processes: the electron spin resonance and the nuclear magnetic resonance method, and gamma-resonance spectroscopy (V. V. Voevodskii, V. I. Gol'danskii, L. A. Blyumenfel'd, V. B. Kazanskii, and others).

The electron spin resonance method, discovered by the Soviet physicist E. K. Zavoiskii at Kazan', has become standard all over the world for the detection and structural investigation of free radicals formed as reaction intermediates or in other ways.

The Institute of Chemical Kinetics and Combustion of the Siberian Section of the Academy of Sciences of the USSR is extensively studying the kinetics and mechanism of chain and radiation-chemical reactions. The kinetics of chemical change in gaseous and condensed media are being investigated.

M. G. Gonikberg is making interesting studies in the field of chemical kinetics at the Institute of Organic Chemistry.

This work is mainly aimed at the effect of pressure on the rate constants of liquid-phase reactions. One of the most important results obtained is the conclusion, based on extensive experimental data, that the accelerating effect of pressure increases as the reaction becomes more sterically hindered. The reason for this is the partial overlapping of the van der Waals spheres of the atoms which screen the reaction centres in the activated complex: thus, additional compression becomes possible during the formation of the activated complex. These results were the basis of a proposed new method for studying the structure and properties of the transition state and the mechanism of organic reactions by kinetic studies at high pressure.

Beginning in the second half of the 1950's, many investigations have been devoted to the kinetics of polymerisation processes. Lack of space compels us to mention only a few of these.

The pioneer in this field was S. V. Lebedev, who studied the kinetics of the polymerisation of diene and allene hydrocarbons in the late 1920's.

S. S. Medvedev and his school (Kh. S. Bagdasaryan, A. D. Abkin, A. R. Gantmakher, and others) made an important contribution to studies of polymerisation processes. By treating polymerisation on the basis of chain reaction theory they put forward the fundamental view that polymerisation processes occur through free radicals. This led to an understanding of the chemical nature of the elementary stages of polymerisation and copolymerisation processes.

Much effort was devoted in Medvedev's work to the kinetics of anionic and cationic polymerisation, and also to coordination polymerisation of hydrocarbon and polar monomers.

Some important contributions to polymerisation kinetics were made by B. A. Dolgoplosk, whose scientific output was aimed primarily at the chemistry of synthetic rubber. In particular, much of his work was connected with the oxidation–reduction initiation of radical chain polymerisation, cross-linking, and degradation processes in polymers.

V. A. Kargin and his school are widely known for their fundamental studies of the structure and properties of polymers in a condensed phase and in solution. During the past 10 years Kargin, working in the Department of High-Molecular-Weight Compounds of the Chemistry Faculty of Moscow State University and at the Institute of Petrochemicals Synthesis, has carried out studies aimed at finding new methods of synthesis of macromolecules and at controlling polymerisation processes. This work was largely based on the methods of chemical kinetics.

In recent years, studies of the kinetics of polymerisation processes have attracted a great deal of attention at the Institute of Chemical Physics.

A detailed study of the kinetics and mechanism of the ionic polymerisation of monomers containing a heteroatom, made in the laboratory of N. S. Enikolopov, led to the discovery of a new elementary act (chain transfer with chain breaking).

At the same Institute, N. M. Chirkov has been studying since 1958 the polymerisation and copolymerisation processes of alkenes on complex catalysts. A. A. Berlin demonstrated, in his studies of the three-dimensional polymerisation of oligoacrylates, the essential role of the relative decrease in the chain breaking and chain growth constants with increasing viscosity of the medium during the course of the reaction.

Investigations of combustion and explosion processes are closely linked with work in the field of chemical kinetics. Scientists from the Academy of Sciences made important contributions to the development of this area: these include the thermal theory of flame propagation (developed by Ya. B. Zel'dovich, D. A. Frank-Kamenetskii, and N. N. Semenov, 1939–1948) and the theory of detonation developed by Zel'dovich in 1940. The thermal theory of combustion is the most systematic in taking account of the kinetics of the chemical reaction at the combustion front, of the heat transfer processes, and of diffusion. In some of the simplest examples the thermal theory gives a simple analytical expression for the rate of normal combustion, which is a great advance over alternative theories of flame propagation and allows the main rate-determining factors of normal combustion to be identified. The thermal theory is also applicable to combustion in condensed systems: it was shown experimentally in the case of explosives (by A. F. Belyaev of the Institute of Chemical Physics, 1938) that combustion is preceded by evaporation or sublimation of the combustible condensed material.

The first contributions to the theory of turbulent combustion came from the Soviet school of physical chemistry.

The theory of detonation formulated by Zel'dovich is based on the assumption of negligible heat conduction during flame propagation by detonation, which implies a definite structure of the detonation wave front. Zel'dovich specially stressed the role of the chemical (kinetic) factor in the phenomenon of detonating combustion. An important instance of detonation (spherical detonation) was discovered by S. M. Kogarko, who also noted the broadening of the detonation limits in wide-bore tubes and made numerous contributions to safety techniques. Special combustion régimes were discovered and investigated by K. I. Shchelkin and his coworkers.

Comprehensive studies of the main characteristics of explosion and of explosives were published by V. K. Bobolev, P. F. Pokhil, A. Ya. Apin, F. I. Dubovitskii, and others.

At the same Institute, A. S. Sokolik and A. N. Voinov (1936) proposed and exhaustively investigated a new method of ignition of the fuel mixture in internal combustion engines: mixing-chamber flame ignition. This method offers a lower specific fuel consumption and considerable economy. At present, the Institute (L. A. Gussak) in cooperation with workers in industry has developed a new type of automobile mixing-chamber engine. The results of this work are being exploited in the motor-car industry of the country.

CATALYSIS

In the field of catalysis, Soviet science can claim important and universally recognised achievements.

Studies in catalysis developed in parallel with studies in other ancillary areas (chemical kinetics, thermodynamics, adsorption, solid-state theory).

At present, catalytic reactions form the basis of most modern industrial chemical and petrochemical processes, in particular large tonnage processes such as cracking and reforming, and the preparation of many products and intermediates of heavy organic synthesis by oxidation, dehydrogenation, dehydration, isomerisation, alkylation, dealkylation, etc. Studies of the reactions of hydrocarbons contained in natural gas or formed during petroleum refining are of great importance in present-day chemistry.

These investigations have given rise, during the last few decades, to a new branch of the chemical industry—petroleum chemistry, which is producing many hundreds of valuable products second to none in their practical importance.

The extensive development in a short time of this new branch of the chemical industry was made possible first and foremost by the vast scientific effort of the Soviet school of organic chemists working on catalysis under the direction of N. D. Zelinskii. The work of this school was wholly aimed at the catalytic conversions of hydrocarbons: the broad outlines of this work were very clearly described by Zelinskii in his paper read before the session of the Academy of Sciences in 1936, entitled "Contact Phenomena and Changes in the Chemical Nature of Hydrocarbons"[18]. Zelinskii's school included A. A. Balandin, B. A. Kazanskii, N. I. Shuikin, and later A. F. Plate, A. M. Rubinshtein, L. Kh. Freidlin, Kh. M. Minachev, R. Ya. Levina, M. B. Turova-Polyak, S. R. Sergienko, Ya. T. Eidus, and many others. The work of this school (mostly associated with the Zelinskii Institute of Organic Chemistry and Moscow State University) was largely devoted to the study of organic reactions. In this review we shall consider only the physicochemical aspects of this work.

One of Zelinskii's closest collaborators, Balandin, proposed and extensively developed the multiplet theory of catalysis, which to a considerable extent set the pattern of Soviet work in the field of organic catalysis. This theory (whose basic premises were published as long ago as 1929)[19] combines modern views on the structure of matter with the theory of the structure of organic compounds, and can satisfactorily explain the catalytic transformations of organic compounds. Balandin showed that the elementary catalytic act is possible only for some definite ratios of the interatomic distances in the reactant molecules and in the crystal lattice of the catalyst (structural correspondence principle). He also explained the role of factors such as the energy of the bonds which are formed and broken during the reaction, the adsorption potentials, and the heats of reaction (energy correspondence principle).

These principles enable us to take account of the specific features of a catalytic reaction and of the catalysts needed to carry it out, and offer the possibility of predicting the behaviour of a molecule on a catalyst surface.

Besides this work, Balandin and his coworkers also made substantial contributions to the study of the kinetics of heterogeneous catalytic reactions.

Among other activities at the Institute of Organic Chemistry on the physicochemical aspects of heterogeneous catalysis, we must mention first of all the work of A. M. Rubinshtein and his coworkers on the topochemistry of catalysts, on the influence of phase composition, degree of dispersion, and crystal lattice distortions on the catalytic properties and on the texture of catalysts, the detailed investigations of the origin of catalysts, and the work on developing methods of catalyst preparation, etc.

The work of Kh. M. Minachev and coworkers on the catalytic properties of rare-earth elements, and on the use of various types of synthetic zeolites as hydrocarbon isomerisation and alkylation catalysts, is also very important.

Another great theoretical achievement of Soviet scientists in the field of heterogeneous catalysis is the electronic theory. The pioneer of the emphasis on electronic aspects in Soviet physical and inorganic chemistry was L. V. Pisarzhevskii[20], to whom are credited the now familiar definition of oxidation as the loss of an electron, the earliest experiments on the effect of radiation on catalytic reactions, the suggestion that the electrons of the catalyst take part in the catalytic reaction, and the correlation of the electronic properties of solids with their catalytic properties[21].

The foundations of the electronic theory of catalysis were laid by S. Z. Roginskii. The theory states that electrons from the catalyst take part in oxidation–reduction reactions, and the catalytic activity is related to the electronic structure of the catalyst. It was an obvious development to proceed from the postulated link between the catalytic activity and the electronic structure of solids to a study of the semiconductor nature of catalysts. These developments led Roginskii (together with F. F. Vol'kenshtein) to the electronic theory of catalysis at semiconductors, and to the discovery (with O. V. Krylov) of new types of redox catalysts. The application of the electronic theory to the mild oxidation of hydrocarbons and to the ammonia synthesis has resulted in significant improvements in existing catalysts and in the possibility of further development in these important industries (Institute of Chemical Physics, Institute of Physical Chemistry).

The work of Roginskii and his collaborators (O. V. Krylov, L. Ya. Margolis, G. M. Zhabrova, and others) has established new rules relating the catalytic activity of solids to the position of their elements in the Periodic Table, and relating catalytic properties to semiconductor properties, to the peculiarities of the catalytic spectrum, and to the choice of catalyst.

Another important result associated with the name of Roginskii is his very recent proposal to carry out catalytic reactions in a chromatographic régime. In this method the catalytic conversion of the reactants in the reactor is combined with chromatographic separation of the products. Higher conversion efficiencies can be achieved than under normal conditions, and significantly lower reaction temperatures are possible. Furthermore, the desired product can be obtained in a higher state of purity. Subsequently, Roginskii and Yanovskii proposed a method for carrying out catalytic reactions in a pulsed chromatographic régime which allows catalysts to be assessed much faster on the laboratory and pilot-plant scale.

Another interesting aspect is the hypothesis put forward by N. N. Semenov, V. V. Voevodskii, and F. F. Vol'kenshtein that adsorbed free radicals have an important part to play in heterogeneous catalysis: the corollary is that catalytic reactions can proceed by a chain mechanism. Although it was subsequently shown that chain reactions are less common in catalysis than had originally been thought, the prediction was confirmed in a number of instances (compare the work of Ya. T. Eidus on the catalytically initiated hydropolymerisation of alkanes, Roginskii's work on the Fischer–Tropsch synthesis, etc.). However, the study of adsorbed free radicals has attracted a great deal of interest in recent years in connection with the extensive development of ESR work. In many instances it has been possible to examine in detail the structure and properties of adsorbed free radicals, and to demonstrate their key role in adsorption, catalysis, and radiation catalysis processes (V. B. Kazanskii).

Studies in the field of catalysis are developing successfully at the newly created Institute of Catalysis of the Siberian Section of the Academy of Sciences of the USSR, led by G. K. Boreskov.

Boreskov was responsible for fundamental investigations on the theory of catalysis and on the scientific foundations

of the practical application of catalytic reactions. He introduced the concept of specific catalytic activity and showed that this quantity is approximately constant for most catalysts. Using tracer techniques, he developed methods for measuring the energy of the bond between the reactants and the catalyst, and demonstrated the importance of this parameter in the prediction of catalytic activity, he published a number of major investigations of the kinetics of catalytic reactions, and he gave a general formulation of the importance of interactions between the reaction mixture and the catalyst.

The Institute has formulated the principles which control the preparation of catalysts with an optimum pore structure: as a result, a new catalyst for the production of sulphuric acid giving a twofold increase in reaction rate has been developed.

Studies of model reactions and of the optimisation of catalytic processes, aimed at shortening the time between laboratory investigations of catalytic reactions and industrial exploitation, claim a significant part of the work of the Institute.

M.I.Temkin (Karpov Institute) put forward the theory of reaction kinetics at inhomogeneous surfaces. He proposed a logarithmic adsorption isotherm (the Temkin isotherm) which is widely used all over the world in work on chemisorption, heterogeneous catalysis, and electrochemical kinetics. By using this isotherm, Temkin was able to derive theoretically valid kinetic equations for a number of industrial catalytic processes. The first example of the fruitful application of these ideas was the development of a theory for one of the most important processes of chemical technology—the synthesis of ammonia. Temkin also established the kinetics and the mechanism of other important processes, such as the conversion of carbon monoxide, the gasification of coal, isotope exchange, the oxidation of ammonia and ethylene, the hydration of acetylene, and the hydration of ethylene.

The work of Temkin on the kinetics of catalytic processes is being widely applied in the design of catalytic plant and in the optimisation of processes with the help of electronic computers. The flow-circulation method, which offers a number of advantages for experimental studies of the kinetics of heterogeneous catalytic reactions, was suggested by Temkin. His contribution to the development of the general foundations of the kinetics of multistage chemical reactions was also a major one.

Mention must also be made of the large effort at the Institute of Petrochemical Synthesis on thermocatalytic methods for refining petroleum and petroleum products (K.P.Lavrovskii) and on the catalytic production from petroleum hydrocarbons of higher fatty alcohols suitable for the preparation of wetting agents (A.N.Bashkirov and V.V.Kamzolkin).

In recent years the Institute of Physical Chemistry (P.A.Rebinder and E.D.Shchukin) has worked on the principles underlying the control of the mechanical stability of catalysts by applying the concepts of physicochemical mechanics. In particular, they were able to increase the strength of the bismuth–molybdenum catalyst used for the oxidative dehydrogenation of propene and butene.

During the period of Soviet rule, a large number of catalytic investigations was carried out at Moscow State University. In the mid-1920's E.I.Shpital'skii (followed by N.N.Petin and N.I.Kobozev) developed and established experimentally the theory of intermediate compounds in homogeneous catalysis. In 1939 Kobozev proposed the theory of active ensembles. The theory of the kinetics of reactions under flow conditions was developed by the work of A.V.Frost and G.M.Panchenkov. Frost and Panchenkov, with K.V.Topchieva, successfully investigated catalysis on alumina–silicas.

We cannot ignore the contribution of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR (A.I.Brodskii and V.A.Roiter) to studies of the mechanism of catalytic reactions by the tracer atom method, or that of the Kazakh University (D.V.Sokol'skii) to the development of continuous catalytic hydrogenation of vegetable fats at low temperatures.

Sokol'skii developed new methods of investigation and control for hydrogenation catalysts, and in particular he discovered an interesting new phenomenon: the sharp decrease in electrical conductivity of a catalyst moistened with solvent upon removing the adsorbed hydrogen.

All these researches, together with some others in the field of heterogeneous catalysis, provided a wealth of information on the kinetics of heterogeneous reactions and on methods for investigating these reactions, on the theory of topochemical processes, and on the statistics of non-uniform surfaces. Lastly, the calculations needed in industrial processes involving heterogeneous catalysis were greatly assisted by the original and intensive development of the macroscopic kinetics of heterogeneous processes in the USSR, including diffusion kinetics, physicochemical hydromechanics, the calculation of thermal régimes, and the theory of reactions in a fluidised bed (V.G.Levich, O.M.Todes, D.A.Frank-Kamenetskii).

The work of Levich was a fundamental contribution to this field of research: he even proposed the term "physicochemical hydrodynamics" for the branch of science which deals with the multiplicity of problems presented by the effect of the motion of liquids and gases on chemical reactions and the influence of physicochemical factors on the motion of liquids. Levich and his coworkers developed a theory of convective diffusion and heat transfer in turbulent liquid flow, a theory of the elementary act in liquid extraction and gas scrubbing, and methods of solving mass- and heat-transfer problems in a static or fluidised granular bed. The pioneering work on diffusion kinetics in the USSR was done by Frank-Kamenetskii, but Yu.S.Elovich and O.M.Todes also made contributions in this area.

M.F.Nagiev, Yu.G.Mamedaliev, and S.D.Mekhtiev (Academy of Sciences of the Azerbaidzhan SSR) investigated the kinetics of industrial systems, mainly with a view to developing improved methods of petroleum refining.

The volume of work on homogeneous catalytic reaction in our country is also very considerable, but relatively little research has been aimed specifically at the mechanism of homogeneous catalysis.

Thus, the Institute of Chemical Physics has developed, from its studies of the kinetics and mechanism of slow, liquid-phase alkene oxidation reactions, a method for the production of acetic acid, ethyl methyl ketone, and ethyl acetate by the oxidation of compressed butane, and also a promising method of preparation of alkene oxides by the simultaneous oxidation of alkenes and other organic compounds in the liquid phase.

E.A.Shilov (Academy of Sciences of the Ukrainian SSR) has made valuable contributions to the study of homogeneous catalytic reactions.

The problem of homogeneous catalytic synthetic reactions with organometallic complex catalysts is of intrinsic interest. These catalysts are widely used in the chemistry of high-molecular-weight compounds. We shall mention only the work at the Institute of Organoelemental Compounds, which demonstrated in principle the possibility of the fixation of atmospheric nitrogen by means of compounds of this type (M. E. Vol'pin), and similar work at the outstation of the Institute of Chemical Physics (E. A. Shilov).

ELECTROCHEMISTRY

The earliest electrochemical work in our country is associated with the names of M. V. Lomonosov, V. V. Petrov, F. F. Grotthus, B. S. Yakobi, E. Kh. Lents, A. S. Savel'ev, A. P. Sokolov, and others.

With the Soviet era, broad and comprehensive development began; this allowed Soviet electrochemistry to occupy one of the leading positions in world science.

The interest in electrochemical problems, and particularly in electrochemical kinetics, grew even stronger in the following years.

The work done in our country (initially, at the Academy of Sciences) on the theory of the electrical double layer, on the influence of adsorption on the kinetics of electrode processes, on the role of diffusion factors, on the theory of hydrogen overpotential, on the quantum-mechanical theory of electrode processes, on the electrochemical theory of corrosion and passivity, on the mechanism of metal electrodeposition, and on fused salt electrochemistry all played a major role in developing the theoretical foundations and the experimental methods of modern electrochemistry [22,23].

The establishments engaged on the solution of these problems include: the Institute of Electrochemistry of the Academy of Sciences of the USSR, the Institute of Physical Chemistry of the Academy of Sciences of the USSR, the Institute of Electrochemistry of the Urals Section of the Academy of Sciences of the USSR, the Institute of Physical and Organic Chemistry of the Academy of Sciences of the USSR (Kazan'), the Institute of Chemistry of the Academy of Sciences of the Lithuanian SSR, the Institutes of the Academy of Sciences of the Ukrainian SSR, the Karpov Physicochemical Institute, and many universities.

The most important electrochemical school in our country is the school of A. N. Frumkin, whose activities were associated at various times with the Karpov Physicochemical Institute, the Institute of Physical Chemistry of the Academy of Sciences of the USSR, and since 1958 with the Institute of Electrochemistry of the Academy of Sciences of the USSR [24].

Frumkin and his coworkers (B. N. Kabanov, R. Kh. Burshtein, N. A. Bakh, Ya. M. Kolotyrkin, M. A. Proskurnin, O. A. Esin, B. V. Ershler, V. I. Veselovskii, P. D. Lukovtsev, P. I. Dolin, Z. A. Iofa, V. S. Bagotskii, B. B. Damaskin, and others) started from the assumption that a close link exists between the mechanism of an electrochemical process on the one hand and the structure and electrochemical properties of metal surfaces and of the metal–solution interface on the other hand. Their theoretical and experimental work, for which new methods had to be developed, has added considerable depth to our understanding of the structure of these interfaces, and in particular they have allowed us for the first time to identify the correct value of the double layer capacitance and to correlate adsorption from solutions with the appearance of potential jumps at the electrode. They provided a solution for the so-called Volta problem (which had occupied electrochemists since the beginning of the previous century) regarding the relationship between the electromotive force of a galvanic cell and the contact potentials which appear when the metals are placed in contact in a vacuum.

The zero-charge potential was introduced into electrochemistry as a factor defining the adsorption properties and many electrochemical properties of metals, and various methods of measuring this potential were developed.

The work of the Soviet school of electrochemists has made possible some striking advances in our theoretical understanding of the structure of the electrical double layer. A paper by Frumkin published in 1919 gave a thermodynamic derivation and a test of the basic equation of electrocapillarity, by means of which the charge on the electrode and the adsorption of various components from the solution on the electrode surface can be calculated from measurements of surface tension. The electrocapillarity method was used to investigate the electrical double layer in non-aqueous solutions. Subsequently, electrocapillarity measurements and measurements of electrode capacity were widely used by Soviet electrochemists in studies of the electrical double layer on many liquid and solid metals.

The work of O. A. Esin, B. V. Ershler, and V. G. Levich contributed significantly to the development of double layer theory.

This school established the mechanism and the kinetics of some important electrode processes, such as hydrogen evolution, the evolution and the reduction of oxygen, and the reduction of chlorine in a number of anions and organic compounds; they showed that in many instances the rate of the overall process is determined by the rate of the electron transfer stage (from the metal surface to the reacting species).

Ershler and P. I. Dolin showed that the rates of fast electrochemical reactions can be measured by using alternating current: this was the first step towards the measurement of electrode processes under non-stationary conditions.

All this work played a major part in the creation of a new branch of chemical science—electrochemical kinetics—and provided a bridge linking electrochemistry to colloid chemistry, adsorption theory, catalysis theory, etc.

More recently, Levich developed the first physically sound theory of diffusion in moving liquids and of matter transport to the electrode surface, which enables the maximal current to be calculated under given conditions of mixing. On the basis of this theory, he proposed the rotating disc electrode as a tool for studying diffusion phenomena in electrochemical processes: this electrode is now widely used both in this country and abroad. Workers at the Institute of Electrochemistry of the Academy of Sciences and in the Department of Electrochemistry of Moscow State University developed a theory of the structure of the double layer on platinum group metals (A. N. Frumkin, N. A. Balashova, and O. A. Petrii), discovered a new form of discharge (which they termed barrierless discharge), and published the first experimental determination of an important constant—the adsorption energy of a hydrogen atom on a mercury electrode surface (L. I. Krishtalik).

Among the theoretical work on the electrochemistry of organic compounds we must mention also an extensive

series of investigations of electrolytic reduction reactions involving the participation of adsorbed organic molecules, carried out at the Institute of Electrochemistry of the Academy of Sciences (G. A. Tedoradze) and at the Institute of Organic Chemistry of the Academy of Sciences (S.G. Mairanovskii).

Theoretical electrochemistry provides the foundations for the solution of a number of problems of major importance to the national economy. A problem of the utmost importance is the realisation of fuel cells—devices in which the chemical energy of the fuel can be directly converted into electrical energy. Fuel cells are already used in astronautics: in the relatively near future we can expect to see them used in transport and in a number of specialised applications, and later perhaps in power generation. The pioneering work in this field in the Soviet Union was done by O.K. Davtyan of the Energetics Institute of the Academy of Sciences of the USSR. In recent years success was reported in studying the mechanism of processes taking place in fuel cells. Model systems have been analysed and a theory of porous electrodes was developed to allow their surface to be used efficiently (Institute of Electrochemistry of the Academy of Sciences, Karpov Institute, Odessa State University, Dnepropetrovsk Institute of Chemical Technology). The most satisfactory method (disc electrode with a ring) was developed for studying the electrolytic reduction of oxygen at the positive electrode of a fuel cell (Institute of Electrochemistry and Moscow State University). Progress is being made on the mechanism of electrolytic oxidation of organic compounds likely to be used as electrochemical fuels (Institute of Electrochemistry). A theory of the electronic conduction of solid electrolytes in equilibrium with a gas phase has been developed to describe the operation of fuel cells based on these electrolytes (Institute of Electrochemistry of the Urals Section of the Academy of Sciences of the USSR).

A great deal of interest attaches to the recently developed electrochemical transducers (memory cells, integrators, pressure and acceleration detectors, etc.) which effectively complement semiconductor devices in the low-frequency and the low-signal-power field. These devices are particularly suited for use in learning and self-organising systems. Various transducers have already been developed, including electrochemical transmitters capable of detecting mechanical vibrations with a sensitivity often orders of magnitude greater than that of existing systems, notwithstanding their much smaller size (P. D. Lukovtsev, Institute of Electrochemistry, and N. S. Lidorenko, All-Union Scientific Research Institute for Fuel Utilisation).

Research is in progress on advanced electrochemical methods of metal treatment: electrochemical machining, based on intensive anodic dissolution at high current densities, and electrochemical polishing. These methods are often more effective, faster, and cheaper than mechanical methods, particularly for very hard and refractory alloys {TsNIMS [Central Research Institute for Mechanical Construction? (Ed. of Translation)], Institute of Electrochemistry}. The mechanism of these processes has been investigated, and the role of kinetic and ohmic factors identified. The collaboration between industry and the Academy of Sciences produced excellent results in this instance.

Among the contributions of the institutes of the Academy of Sciences, mention must be made of the work of the Institute of Organic and Physical Chemistry on electrodeposition, anodic dissolution, and electropolishing of metals (G. S. Vozdvizhenskii) and of the work of the Institute of Physical Chemistry on the electrodeposition of metals.

The work of K. M. Gorbunova and P. D. Dankov on the mechanism of crystal growth and on nucleation processes during electrolysis was a pioneering effort. It was followed by numerous important investigations of the electrodeposition of alloys at the Institute of Physical Chemistry (K. M. Gorbunova and Yu. M. Polukarov), of the growth mechanism of dendrites during electrolysis, of the influence of adsorbed foreign materials on the electrodeposition of metals, and of the effect of temperature on the behaviour of electrodes with a slow exchange step (A. T. Vagramyan and coworkers).

At the Mendeleev Institute of Chemical Technology, the kinetics of electrode processes has been investigated over a wide range of temperatures (S. V. Gorbachev), the mechanism of electrochemical dimerisation has been examined in connection with the problem of electrolytic synthesis (M. Ya. Fioshin), new methods of electroplating have been developed, and their mechanism has been investigated (N. T. Kudryavtsev). More recently, the mode of action of levelling agents has been examined (S. S. Kruglikov).

Studies of electrochemical kinetics in fused salts are of great importance both from the practical and the theoretical point of view. The earliest work of this type was reported by S. V. Karpachev in the 1930's. O. A. Esin made systematic polarisation measurements in fused slags, M. V. Smirnov and S. I. Rempel' in halides. These researches showed that although the majority of chemical reactions are diffusion-controlled at high temperatures, slow discharge processes are also observed in some instances (for example, hydrogen evolution.

All the main data on the structure of the electrical double layer at the boundary between fused metals and electrolytes have also been established in our country (S. V. Karpachev, A. T. Stromberg, V. A. Kuznetsov, E. A. Ukshe).

Yu. K. Delimarskii and other Ukrainian electrochemists developed the polarography of fused salts and studied the specific features of diffusion-controlled kinetics in the same media. One important result of this work was to show that solid electrodes can be used for polarography, and also the application of polarography to the study of complex formation in melts.

Mention must be made also of the recently developed studies of the kinetics of electrodeposition from fused salts (K. M. Gorbunova of the Institute of Physical Chemistry, M. V. Smirnov of the Institute of Electrochemistry of the Urals Section of the Academy of Sciences, and others). In this work, which was primarily aimed at the electrolytic production of refractory metals, phenomena such as the dependence of the number of crystallisation centres upon the electrolysis parameters were first discovered and investigated in fused salts.

The study of corrosion processes is an aspect of electrochemistry of great practical importance. The basic studies of corrosion processes and of corrosion protection were started by V. A. Kistyakovskii at the Academy of Sciences; the work of N. A. Izgaryshev also contributed to the early development of corrosion science. The study of corrosion processes began to develop very rapidly as a result of the work of G. V. Akimov and his students (N. D. Tomashov, I. L. Rozenfel'd), who developed the theory of multi-electrode systems to predict the corrosion behaviour of each

constituent of a complex system, to investigate structural corrosion and the role of local cells, to explain the mechanism of corrosion in the presence of atmospheric oxygen, and to study the nature and protective properties of oxide films[24].

A. N. Frumkin, Yu. M. Kolotyrkin, Ya. V. Durdin, and others established the mechanism of corrosion of uniform metal surfaces, thus creating a bridge between corrosion theory and electrochemical kinetics.

As well as solving the above theoretical corrosion problems, the corrosion scientists of the Academy of Sciences contributed to the solution of many practical problems in the fields of atomic energy, aircraft and rocket design, shipbuilding, and the chemical and petroleum industry.

At the Institute of Physical Chemistry, the main centre of corrosion studies of the Academy of Sciences, many important investigations were carried out. Various coatings were tested, some of which have been adopted for the national network of pipelines, including the "Druzhba" oil pipeline. Electrochemical protection methods for underground and submarine equipment were developed and widely exploited. New gas pipelines were provided with protective devices. A new method of protection against stray currents, relying on the simultaneous use of protectors and germanium rectifiers, has been proposed and is being introduced into industrial practice. A new class of compounds has been synthesised (salts of amines and nitrobenzoic acids) with strongly corrosion-inhibiting properties towards both ferrous and non-ferrous metals. New methods of protection of components and complicated structures by volatile and contact inhibitors have been developed and handed over to industry. The scientific principle of corrosion resistant alloys based on titanium and zirconium and offering high-grade mechanical and anticorrosion properties have been proposed. The methods of protection of building structures developed at the Institute have been adopted and specified by the Department of State Construction.

A method of deposition of thin ferromagnetic films by chemical nickel plating has been worked out. The films produced in this way show a low coercive force and can be used for magnetic screening of complicated radio components. The basic features of the electrodeposition of alloys of refractory metals (titanium, tungsten, etc.) have been studied. The formulations and operating conditions proposed for electropolishing have been widely used in the finishing of heat-resistant alloys for aviation engines.

Valuable work in the field of protection against metal corrosion has been done also at the Karpov Institute. Thus, Kolotyrkin investigated the corrosion and electrochemical behaviour of a series of metals and alloys in aqueous media and pointed out the rules controlling their passivation. This work strengthened and stimulated the adsorption theory of passivity, whose foundations had been laid by B. V. Ershler and B. N. Kabanov.

Kolotyrkin's work on the mechanism of passivator action, which led to the formulation of the basic theory of the mode of action of oxidation and cathodic inhibitors, was applied to the solution of many problems of the corrosion stability of metals and alloys at high temperatures and pressure, and also in the presence of energetic radiations. At the present time Kolotyrkin is engaged on the practical exploitation of anodic protection of metals against corrosion.

Kolotyrkin also formulated the basic theory of pitting corrosion, which was confirmed by systematic studies of the dissolution of zirconium, iron, and iron alloys.

Recent work at the Department of Electrochemistry of Moscow State University (V. N. Korshunov) and at the Karpov Institute (Ya. M. Kolotyrkin, T. M. Florianovich) has shown that metal corrosion in aqueous solutions may occur not only by an electrochemical but also by a chemical mechanism, that is, without distinguishable anodic and cathodic processes. L. I. Antropov (Kiev Polytechnic Institute) has carried out a major series of investigations on the effect of the point of zero charge on the corrosion behaviour of metals and on the adsorption of corrosion inhibitors.

LIQUIDS. SOLUTIONS

Soviet scientists have always occupied a leading position in the study of solutions. Those who were already highly respected workers at the time of the October Revolution, such as M. S. Vrevskii, I. A. Kablukov, V. A. Kistyakovskii, and D. P. Konovalov, later gathered around themselves younger talent and thus laid the foundations of a number of Soviet schools of physical chemists, some of whose names are now widely known.

We shall mention first of all the work which had the greatest influence on the overall problem. Ya. I. Frenkel' was the first to attempt a systematic phenomenological theory of the liquid state on the basis of the nature of the motion of molecules in liquids. For a given molecule, this motion is determined by the molecular field generated by its surroundings and by its own kinetic energy, it follows a discontinuous path, and is characterised by a mean lifetime in temporary equilibrium positions. The basic ideas evolved by Frenkel' provided the foundations for the work of many authors.

N. N. Bogolyubov developed a general approach to the calculation of the thermodynamic properties of one-component and multicomponent systems from studies of the molecular distribution functions of groups of particles. A statistically consistent method of calculating the thermodynamic properties of strong electrolyte solutions, based on the correlation function and variational derivative method, is now widely used by Soviet and foreign theoreticians to solve stochastic problems. The method has been developed in papers by I. Z. Fisher, who examined in particular its application to problems of liquid structure. V. I. Danilov and his school carried out some fundamental work on an experimental method for determining the structure of pure liquids and solutions.

The most interesting and general result obtained by this method was to demonstrate the presence in liquids of short-range order as found in crystals. In a series of theoretical and experimental investigations, M. I. Shakhparonov developed a method of studying the microstructure of liquids and solutions by radiofrequency, optical, and acoustic measurements. His main result was to show that the positions of molecules fluctuate, causing the local physical properties of liquids to differ from their macroscopic values. A. V. Storonkin established by a formal thermodynamic analysis the possible types of phase equilibrium curves in heterogeneous multicomponent systems, including the vapour phase.

A series of papers by I. R. Krichevskii on phase transformations in solutions of non-electrolytes under high pressure made an important contribution to a correct understanding of the relationship between particle–particle interactions and the thermodynamic properties.

Many important results were obtained in the field of electrolyte solution theory. V.K. Semenchenko first put forward the view that ion pair formation affects the behaviour of electrolyte solutions, and gave a physical model of the phenomenon and an approximate mathematical treatment. A similar hypothesis was independently put forward, somewhat later, by Bjerrum, but improvements to his mathematical treatment are still being proposed. S.V. Tyablik and V.V. Tolmachev showed, by Bogolyubov's correlation function method, that the Semenchenko–Bjerrum correction for ionic association is obtained automatically when the free energy of an electrolyte solution is calculated by a systematic statistical approach. V.G. Levich and V.A. Kir'yanov used Bogolyubov's method to derive the most general expression for the free energy of an electrolyte solution, in which the Coulombic potential at small distances is replaced by an arbitrary potential. The expression obtained can, according to the form of the potential chosen, describe purely Coulombic interaction or alternatively it can describe the Brønsted–Guggenheim "specific" interaction of ions with a non-Coulombic short-range interaction. Yu.M. Kossler discussed the physical principles underlying the non-Coulombic components of the potential. G.I. Mikulin proposed a numerical method of solving the Poisson–Boltzmann equation in which account is taken of the variation of the dielectric constant with distance from the centre of the ion. This method is strictly accurate, unlike some even more recent work by various foreign authors.

The thermodynamics of ion solvation has made significant progress through the efforts of a number of scientists. V.A. Pleskov put forward the idea that the solvation energies in different solvents must tend towards a common value as the radius of the ion increases. Hence, by choosing an electrode reversible to the ion for which these energies are practically equal it is possible to compare the chemical solvation energies of various ions (which are not experimentally measurable). His researches with a series of non-aqueous solvents showed that caesium or rubidium can be used as the electrode. A.F. Kapustinskii had some interesting views on the difference between the true radii of ions in aqueous solutions and their crystal-chemical radii. His corrections (±0.28 Å) were applied by N.A. Izmailov to resolve the total hydration energy into its components for ions. Unlike others who made similar attempts, Izmailov suggested extrapolating the sums and differences of the solvation energies of a given ion with a number of other ions of increasing radius to infinite ionic radius. This method is independent of any hypothesis on the structure of solutions. K.B. Yatsimirskii made valuable studies of specific aspects of the energy of formation of ions, of proton affinity, and of ion hydration.

Problems of the structure of electrolyte solutions are attracting a great deal of attention at the moment in the USSR. This work is largely associated with the name of Kapustinskii, who used Fowler and Bernal's tetrahedral model of the water structure in his study of the heat capacity of ions in aqueous solutions and showed that the structure of the solvent must be considered when discussing the thermal motion of ions. O.Ya Samoilov perfected the tetrahedral model by allowing for partial filling of the holes in the ice-like skeleton by water molecules set free by its thermal motion and, by using the ideas of Frenkel', he constructed a consistent model of the structure of water solutions and of the hydration of ions. His concept of positive and negative hydration proved very fruitful in allowing structural and thermodynamic approaches to be unified (for example, the distribution of an electrolyte between water and an immiscible solvent). A series of contributions by K P. Mishchenko and coworkers used the thermodynamic relative partial molal properties to characterise the structure of electrolyte solutions. The specific intersection of composition–property isotherms led Mishchenko to introduce the concept of a real solvation boundary, which reflects the structural and energetic aspects of the process.

A large group of papers by V.A. Plotnikov and his students, who studied the physicochemical and electrochemical properties of a wide range of non-aqueous solutions, forms a slightly isolated topic. Their main contribution was to demonstrate the relationship between these properties and complex formation, and a vast fund of factual data on the cathodic deposition of metals.

Studies of solutions under extreme conditions (temperatures up to 400°C) were undertaken on a broad scale for the first time in the USSR by I.S. Galinker. These studies produced interesting experimental results, relevant to an understanding of the structural properties of water.

The glass electrode, whose theory was developed in detail by B.P. Nikol'skii, plays an important part in measurements of the electrode potentials of hydrogen and alkali metal ions, which are needed in thermodynamic calculations Techniques for the preparation of glass electrodes suited to different types of measurement were also developed in Nikol'skii's laboratory.

The theory of acids and based was considerably developed by the work of A.I Shatenshtein, N A Izmailov, and M.I. Usanovich. Shatenshtein and Usanovich broadened and generalised the concept of acids and bases so as to include acid–base interactions not involving ionisation. This allowed them to include reactions not considered in Brønsted's previous scheme, to introduce the concept of acid-like aprotic substances and to show that the acidic (or basic) properties of a substance depend to a considerable extent on the protonophilic (or acidic) properties of its reaction partner. Izmailov discovered and investigated the influence of solvent on the relative strength of acids and bases, which results from interactions with the solvent (solvation), and originated unified studies of acidity.

RADIATION CHEMISTRY

Radiation chemistry became a discipline in its own right during the last two decades, coinciding with the practical application of atomic energy.

Our scientists have contributed very significantly to the creation of the theoretical foundations of radiation chemistry by their work on ion–molecule reactions, energy transfer during radiolysis, the radiolysis of aqueous and of organic systems, the formation and transformations of free radicals and ions in irradiated solids, radiation-induced polymerisation in the solid phase, etc.[26-28]

It may now be claimed that radiation chemistry in the Soviet Union is on a level with world radiation chemistry.

The institutes of the Academy of Sciences (Institute of Chemical Physics, Institute of Electrochemistry, Institute of Physical Chemistry, Institute of Petrochemical Synthesis), the Karpov Institute, and the Chemistry Faculty of Moscow State University have all been involved in the development of radiation chemistry.

Studies of the radiolysis of inorganic and organic systems occupy an important place among Soviet researches in this field.

The work on radiation-chemical changes in solid and in liquid organic compounds was done mainly by N. A. Bakh, Kh. S. Bagdasar'yan, M. A. Proskurnin, N. Ya. Buben, L. S. Polak, and V. L. Tal'roze. These workers clarified the role of ions, free thermalised electrons, and free radicals in radiolysis processes in condensed media. The radiolysis products were identified and investigated, and many radiation-chemical changes in organic compounds were characterised quantitatively.

Much of the work on free radicals in condensed phases was done by the ESR method, whose development owes a great deal to Soviet workers. The method allows the detection, identification, and quantitative estimation of free radicals formed as intermediate radiolysis products. This work was done by N. A. Bakh, N. Ya. Buben, V. V. Voevodskii, L. S. Polak, S. Ya. Pshezhetskii, and others.

Studies of radiation-induced oxidation began in 1949 in the Soviet Union, mainly under the direction of Bakh. The first studies were aimed at the determination and identification of the oxidation products of liquid hydrocarbons of different structures. It was shown that the yield depends on the nature of the hydrocarbon and on the irradiation conditions, whereas the mechanism of the processes involved depends on the temperature.

The radiolysis of water and aqueous solutions is the most widely investigated topic in radiation chemistry, because of the extensive use of water in atomic technology and reactor design. The work of the Soviet scientists P. I. Dolin, V. I. Veselovskii, B. V. Ershler, M. A. Proskurnin, and others, in the period 1946–1955, led to the development of the free-radical mechanism of the radiolysis of water independently of foreign workers, who reached similar conclusions.

The sensitising effect of solid surfaces on radiation-chemical processes in liquid systems was discovered by the Soviet scientists L. V. Pisarzhevskii and V. I. Veselovskii. This work is now continuing at the Institute of Petrochemical Synthesis, at the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, and elsewhere; the effect of irradiation on catalytic processes in general is also being investigated (Karpov Physicochemical Institute, Institute of Physical Chemistry, and Institute of Chemical Physics of the Academy of Sciences of the USSR, etc.).

The first papers on the acceleration of topochemical processes by previous treatment by ionising radiation appeared in 1955–1956. In the following years a large number of investigations in this field, carried out under the direction of S. Z. Roginskii, G. M. Zhabrova, and V. V. Boldyreva, were reported.

Systematic studies of the radiation chemistry of polymers were pursued mainly at the Karpov Physicochemical Institute and at the Institute of Physical Chemistry of the Academy of Sciences of the USSR. Initially, this work was aimed at solving problems arising in the use of polymeric materials in the handling and application of radioactive materials. The main effort was directed towards the radiation-induced degradation of polymeric materials and changes in their physico-mechanical properties under the influence of radiation. However, the essential experimental facts about radiation-chemical changes in polymeric systems were established at an early stage and the first views on the nature of the processes involved were put forward.

Subsequently, the effort on various aspects of the radiation chemistry of polymers was extended by the numerous research institutions whose primary interest was to investigate the possible use of radiation-chemical processes for the controlled modification of polymeric materials, principally in the direction of radiation-induced vulcanisation.

V. A. Kargin and V. L. Karpov proposed the use of ionising radiations for vulcanising polyethylene, which could not be vulcanised in any other way. S. S. Medvedev and A. D. Abkin made a detailed study of the radiation polymerisation of various monomers in the liquid and the gas phase. V. I. Gol'danskii's method of cross-linking different monomers by the localised action of thermal neutrons has proved very valuable.

The radiation method offers very wide scope for including polymerisation reactions in the solid phase. A very promising technique has been developed at the Institute of Electrochemistry of the Academy of Sciences of the USSR and at the Institute of Physical Chemistry of the Academy of Sciences of the USSR for gas-phase radiation-induced graft copolymerisation, which allows combined inorganic–organic materials to be prepared as well as sheathed filaments and two-layer films combining the properties of the initial (inner) layer with those of the outer layer formed by the grafted polymer.

A method of improving wood cellulose by impregnating it with various monomers and polymerising them with gamma radiation, proposed in 1958 in the Soviet Union, has achieved great technological importance.

A number of radiation-chemical processes are now fully developed and have reached the stage of pilot-plant production: they include the cross-linking of thermally stabilised polyethylene, the telomerisation of ethylene, the oxidation of paraffins, the sulphochlorination of Synthin [a fuel (Ed. of Translation)], and the production of special-purpose rubbers.

PHYSICAL CHEMISTRY OF SURFACE PHENOMENA. ADSORPTION. CHROMATOGRAPHY

The variation of the properties of colloidal systems with the degree of subdivision of the disperse phase and the stability of these systems were investigated by A. V. Dumanskii (Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR) and by N. P. Peskov. Their conclusions have been widely applied in Soviet soil science as well as in the control side of the food industry.

The rapid growth of the high-polymers industry (plastics, elastomers, viscose, synthetic fibres) has stimulated the development of research on lyophilic colloids, a term which was then applied to polymers in colloidal chemistry. The work of A. V. Dumanskii, S. M. Lipatov, V. A. Kargin, and B. A. Dogadkin[29] is noteworthy in this area. This topic subsequently merged into the developing field of polymer chemistry.

Research on the physical chemistry of surface phenomena is centred at the moment on the Institute of Physical Chemistry, the Karpov Institute, Moscow State University, and some associated institutes.

By 1935, a Disperse Systems Division had been set up at the Institute of Colloidal and Electrochemistry under the leadership of P. A. Rebinder. He and his coworkers (A. B. Taubman, V. I. Likhtman, E. D. Shchukin, and others) developed a number of aspects of modern colloid chemistry, and they also created a new interdisciplinary area of chemical science—the physicochemical mechanics of disperse structures, solids, and technical materials. The features and mechanisms of the formation and development of disperse structures, leading to the synthesis of fine-grained, strong, and durable solids and technical materials, were investigated, as well as the deformation and disintegration of solids of various compositions and degrees of dispersion (from fully dense and strong bodies to finely porous solids of varying and occasionally high porosity[30]).

This work led to many essentially new results of great scientific and economic importance. We note first of all the effect producing easy deformation of solids and decreased strength under the influence of an active medium or low amounts of adsorbed substances (the so-called Rebinder effect). The discovery of this effect led to the development of methods now used under industrial conditions for ultrafine grinding and to the softening solution method for raising the efficiency of drilling in hard rock. New high-efficiency lubricating coolants for the working and cutting of metals were proposed. Scientific foundations were developed for optimising the manufacture of precast concrete and reinforced concrete, and also sand concrete without coarse fillers.

Rebinder developed new physicochemical ideas on the three-dimensional structures arising with disperse and colloidal systems. He established the rheological characteristics of structures of various types, the rules governing their structural and mechanical properties, and methods of controlling these properties. The effect of the interfacial surface energy on the formation of disperse systems—whether involving dispersion or condensation (formation of new disperse phases)—was investigated theoretically and experimentally, including the conditions for spontaneous dispersion. The detailed study of the properties of soap-like surface-active agents (semicolloids of both the ionogenic and the non-ionogenic type) led to the scientific formulation of many valuable applications of surface-active materials in many areas of the national economy (detergents, wetting agents, flotation agents, stabilising and dispersing agents, de-emulsifiers, lubricating coolants, and lubricants, etc.).

Another new development begun in 1935 at the Institute for Colloidal and Electrochemistry under the direction of B. V. Deryagin was the study of surface phenomena with special emphasis on the action of surface forces close to the interface. The extensive investigations made by Deryagin and his coworkers played a fundamental part in the development of the science of surface forces and of their role in the kinetics of physicochemical processes in heterogeneous systems and in colloidal chemistry.

Having discovered and investigated one of the fundamental thermodynamic characteristics of thin layers—the disjoining pressure—Deryagin developed a quantitative theory of the stability of lyophobic colloids. The methods of calculation which he first developed for the repulsion forces arising from the overlapping of ionic atmospheres provided a basis for the currently accepted theory of the stability of lyophobic colloids.

The same laboratory developed a theory of the flotation of mineral particles whose conclusions have been applied practically. Allowance for ion diffusion led to refinements in the modern theory of electrokinetic phenomena, including electrophoresis. The chemical and morphological characteristics of individual soil particles were correlated with the behaviour of soils during application and removal of loads, slip, and filtration. From studies of the physical chemistry of thin water films, a theory was developed to explain the mechanism of migration of moisture and petroleum in porous media.

Deryagin made the first direct measurements of molecular attraction as a function of distance between different solids. His results were subsequently repeated by workers in England and in the Netherlands, and confirmed the modern theory of molecular forces.

Various methods worked out by Deryagin led to the conclusion that the surface of a lyophilic solid can modify the structure and properties of the adjacent layers of liquid to a depth of at least tens of molecular diameters. More recently, previously unknown properties of bulk liquids were discovered as a result of this work.

Researches in the field of aerosols have had far-reaching practical results; in particular, new methods of dispersion and precipitation of clouds and fog have been developed, and very efficient and economical condensation filters for the purification of air in mines have been designed.

At the Institute of Physical Chemistry, A. A. Trapeznikov developed new concepts and exploited methods of investigation and apparatus for the rheology of structured systems, and for studying the combined effects of deformation-resisting properties and relaxation in the pre-stationary stage; he also proposed generalised concepts of fluidity limits. His contribution included studies of the mechanical properties of monolayers and soap films formed by insoluble and by soluble surface-active materials.

A laboratory for colloid chemistry was set up by A. P. Rabinovich at the Karpov Institute in 1924. The relationship between ion adsorption processes and the stability of hydrophobic colloids was studied by electrochemical methods, and the important role of ion exchange at the surface of colloidal particles was recognised. Rabinovich was also responsible for the adsorption theory of development, which now forms the basis of photographic science.

Subsequent work in this laboratory, by V. A. Kargin and Z. Ya. Berestneva, demonstrated the important role of chemical phenomena in the behaviour of colloidal systems. It was found that practically all colloidal solutions contain significant amounts of stabilising electrolytes which react chemically with coagulants, and that dealing exclusively with the physical phenomena which take place during coagulation is too coarse an approximation. Chemical reactions between substances in the colloidal state were found to proceed in true solution by gradual dissolution of the particles.

More recently, the application of electron microscopy has enabled the mechanism of formation of colloidal particles to be identified. The first stage was shown to be the formation of large, usually spherical, amorphous particles which then recrystallise and break down into the very fine crystalline particles typical of colloidal solutions.

I. V. Petryanov-Sokolov of the Karpov Institute carried out comprehensive studies in the physical chemistry of aerosol systems. His work and that of his colleagues on the physicochemical properties of aerosols, extending over many years, proved to be a fundamental contribution to science. They developed quantitative methods for the

experimental study of the degree of dispersion of aerosols which are now widely applied, and which have led to the solution of a number of problems concerning the electrical properties of aerosols.

Petryanov-Sokolov made a detailed study of the stability of undischarged aerosols. A series of researches was devoted to the previously unrecognised problem of the behaviour of the disperse phase of an aerosol when the particles are deposited on the fibres of a filter. This work led to the development of novel, important, and widely used processes.

A. N. Fuks and N. N. Tunitskii did some important work at the Institute on the formation and coagulation of aerosols.

Ya. I. Kogan made some important contributions to the development of experimental techniques for studying aerosols, and of methods, devices, and apparatus for testing under industrial conditions the efficiency of a wide range of aerosol filters.

From their studies of the optical properties of aerosols, Kogan and his coworkers designed highly sensitive nephelometers which are now extensively used. The application of his aerosol flocculation method led Kogan to the discovery of molecular condensation nuclei and to the development of unusually sensitive methods of measuring gaseous impurities in air. This work suggested that molecular counters for gaseous impurities can be designed.

A. M. Amelin made an extensive investigation of all instances of formation of supersaturated vapour. He derived numerical formulae for predicting fog formation, for determining its concentration, and for developing fog prevention measures. He put forward a general theory of the formation of aerosols by condensation which is widely used to solve a variety of practical problems.

A Sorption Processes Laboratory (later, Section), led by M. M. Dubinin, was created in 1946 at the Institute of Physical Chemistry of the Academy of Sciences of the USSR. Its main scientific objective was to formulate and refine the theory of the physical adsorption of gases on porous solids. The activities of this laboratory maintained the continuity and the scientific traditions of the school of N. A. Shilov, one of the pioneers of adsorption studies in our country [31].

Extensive experimental and theoretical studies led to a rational classification of porosity which is at the same time a classification of the sorption processes. A quantitative theory of adsorption was developed for the so-called microporous adsorbents (active carbons, zeolites, etc.). This is the theory of volume filling, which permits calculation (from a limited amount of experimental data) of the parameters of the adsorption equilibrium with a precision beyond the scope of alternative modern theories of physical adsorption. In later work the theory was refined and generalised.

Significant results were obtained in the relatively unexplored but practically important field of the adsorption of mixtures of gases.

In addition to studies of adsorption equilibrium, the Section produced valuable results on adsorption kinetics which led to the solution of important problems in sorption technology. Mention must also be made of the important organising and coordinating role played by the Section in the general stream of scientific and technological research on sorption processes in the USSR. This role was recently formally recognised by the creation of the Scientific Committee on Adsorbents.

The Surface Chemistry Laboratory of the same Institute (A. V. Kiselev) has devoted its main effort to a comprehensive study of the chemistry of adsorbent surfaces and the nature of adsorption interactions. The basic adsorption and gas-chromatographic thermodynamic characteristics for various molecules, including hydrocarbons, have been calculated by the methods of statistical mechanics. Heats of adsorption and heat capacities have been measured in new, highly sensitive calorimeters for a number of important systems. The adsorption energy has been directly correlated with the structure of the adsorbed molecules (including macromolecules).

Work in the field of chromatographic analysis began to develop on a wide front in the USSR in 1946–1949, creating the need for a central institution which would coordinate and unify these investigations. A Chromatography Laboratory was created in 1949 at the Institute of Physical Chemistry of the Academy of Sciences of the USSR under K. V. Chmutov, and in 1950 the Scientific Committee on Chromatography was created. The Laboratory has been responsible for some major developments on theoretical and applied aspects of chromatography, including: the laws governing the statics, kinetics, and dynamics of the chromatographic process, the development and theoretical formulation of methods for separating the rare-earth elements, complex formation in chromatography, the radiation stability of ion-exchange materials, the development of new chromatographic methods (the adsorption–complexing method, the distribution chromatography of inorganic substances), the intensification of chromatographic processes (high temperatures and pressures), theoretical models of chromatographic processes, and the development of the most recent automatic apparatus for chromatography. Much of this work has great practical importance and has influenced industrial practice.

The work of A. A. Zhukhovitskii has contributed significantly to the development of a number of scientific topics: the thermodynamics of surface phenomena, the dynamics of adsorption processes, the theory of chromatography, and new variants of chromatographic analysis. Zhukhovitskii developed the theory of adsorption of mixed vapours and the theory of adsorption from solutions. He also made notable contributions to the theoretical foundations of gas and gas–liquid chromatography, and proposed new methods of chromatographic analysis.

The work on the theory of chromatography by N. N. Tunitskii (Karpov Institute) showed that the diffuseness of chromatographic bands arises from fluctuations in the lifetime of particles in the sorbed state. He developed new calculation methods for sorption separation processes which are relevant to the intensive purification of materials. Tunitskii has proposed a theory of the rate of ion exchange with allowance for the mobility of the ions taking part.

G. V. Samsonov (Institute of High-Molecular Compounds of the Academy of Sciences of the USSR) developed a theory of ion exchange on swelling resins which permits a rational choice of sorbent for the removal of some organic ions from complex mixtures. He synthesised carboxylic acid resins having an enhanced selectivity towards certain organic ions (streptomycin, colimycin). His work in the field of sorption is closely associated with the solution of practical problems in the development of technological methods of separation and purification.

In addition to the wide application of existing procedures and apparatus for gas chromatography, many institutions have contributed to the further development of chromatographic practice. The result of this work was a considerable increase in the sensitivity, generality, precision, and reliability of chromatographic methods. The Instrument Design Bureau of the Institute of Petrochemical Synthesis and that of the Institute of Organic Chemistry have played a major role in the development and practical exploitation of gas chromatography apparatus.

THERMODYNAMICS

Advances having major practical importance have been made in the Soviet Union in the study of the thermodynamic properties of special groups of materials used in modern technology (new fuels, semiconductor materials, rare metals, strong alloys, heat-resisting coatings, hard alloys, etc.).

Ya. I. Gerasimov is the leader of a major centre of thermodynamic research in our country—the Physical Chemistry Department of Moscow State University.

The scientific activities of Gerasimov and his coworkers are mainly aimed at the chemical thermodynamics of non-ferrous metallurgy, the thermodynamics of heat-resistant alloys, metal oxides, and semiconducting compounds. They successfully developed many new methods of measurement and investigation of thermodynamic quantities at high temperatures: this work has had a considerable impact on highly energetic systems and other areas of modern technology.

In the same Department, S. M. Skuratov of the Luginin Thermochemistry Laboratory is making high-precision measurements of the heats of combustion of organic compounds. The laboratory has developed a number of new methods.

The work of M. Kh. Karapet'yants in the field of thermodynamics, carried out at the Mendeleev Moscow Chemical Technology Institute, has gained wide recognition. He leads a new scientific project, involving the development and application of a group of methods, which he had originally suggested, of comparative calculation of the physicochemical properties of various substances and process parameters. These methods make possible the calculation of many physical and physicochemical constants from a limited number of experimental data (reference points). Particularly successful was the application by Karapet'yants of his comparative calculation method to evaluating the properties of homologous series of organic compounds (petrochemical calculations), isotope effects, the properties of complex compounds, the physical and physicochemical properties of semiconductors, silicate glasses, etc.

I. R. Krichevskii (State Institute for the Nitrogen Industry) discovered the new phenomenon of limited miscibility of gas phases and made a quantitative study of it in a number of systems. Equally noteworthy is a series of investigations under his direction of the solubility of gases in liquids under high pressures. Having developed accurate methods of investigation in the difficult high-pressure area up to tens of thousands of atmospheres, Krichevskii and his coworkers made a series of technologically important measurements. They also contributed to the development of the thermodynamics of dilute solutions and provided data for the development of the theory of intermolecular forces.

The problem of chemical equilibrium in complex mixtures at high temperatures is of importance in many fields of technology. We should note the experimental studies of equilibria in the thermal and catalytic cracking of hydrocarbons (A. V. Frost, A. A. Vvedenskii, and others), and the development of methods for thermodynamic calculations of combustion and explosion processes (Ya. B. Zel'dovich, A. N. Gurvich, Yu. M. Shaulov.

In the same general area, we note the work on the systematic statistical calculation of thermodynamic quantities for gases at high temperatures (A. V. Frost, I. N. Godnev, and a group of workers at the Institute of Fossil Fuels and the State Institute for Applied Chemistry).

Among the foremost theoretical investigations, mention must be made of the interesting work on second-order phase transformations (L. D. Landau, V. K. Semenchenko). A. V. Storonkin did some interesting work on solution–vapour equilibria in complex multicomponent systems. D. S. Korzhinskii evolved the theory of heterogeneous equilibria in multi-phase, multicomponent open systems, applicable to geological processes.

Many workers have investigated the thermodynamic functions of specific inorganic compounds, groups of compounds, solutions, and alloys, both in theoretical generalisations and in practical problems (mainly in the field of metallurgy). They include E. V. Britske (Scientific Institute of Fertilisers, Insecticides, and Fungicides), A. F. Kapustinskii, V. A. Sokolov, and N. K. Voskresenskaya (Institute of General and Inorganic Chemistry), A. I. Vol'skii (Mineral Institute for Non-Ferrous Metals and Gold), Ya. I. Gerasimov (Moscow State University), A. A. Zhukhovitskii (Institute of Steel), V. A. Kireev (Karpov Institute of Physical Chemistry), G. V. Kurdyumov (Central Scientific Research Institute for Ferrous Metallurgy), K. P. Mishchenko (Leningrad Chemical Technology Institute), M. M. Popov, K. G. Khomyakov, A. V. Rakovskii, S. M Skuratov, An. N. Nesmeyanov (Moscow State University), A. M. Samarin, N. V. Ageev, I. I. Kornilov (Institute of Metallurgy), and S. A. Shchukarev (Leningrad State University).

PHYSICOCHEMICAL ANALYSIS

Closely related to the thermodynamic investigations are the studies in the field of physicochemical analysis, which was created and widely developed in our country by the efforts of N. S. Kurnakov and his school (N. V. Ageev, V. Ya. Anosov, A. G. Grigor'ev, N. N. Efremov, S. F. Zhemchuzhnyi, V. A. Nemilov, S. A. Pogodin, N. I. Stepanov, G. G. Urazov, I. N. Lepeshkov, and others).

The work of Kurnakov's school has established the general principles of physicochemical analysis, led to new experimental methods, and accumulated and unified a vast amount of experimental information on systems consisting of the most varied components such as metals, oxides, sulphides, salts, organic compounds, etc.

From studies of these equilibrium diagrams, accurate conclusions have been made on the nature of the interactions between the components in the systems and on the nature and stability boundaries of the resulting phases (whether individual compounds or solid or liquid solutions).

The concept of singular points in chemical diagrams, introduced by Kurnakov, has made possible accurate discrimination of the chemical individuality of substances, and

has clarified the distinction between daltonides and berthollides, azeotropes, eutectics, cryohydrates, etc.

We cannot overemphasise the importance of the work of Kurnakov and his students in rationalising pyrometallurgical processes, preparing a large number of important alloys, and exploiting the mineral (particularly salt) resources of our country.

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THE TRANSFORMATION OF HYDROCARBONS WITH MEDIUM-SIZED RINGS IN THE PRESENCE OF PLATINUM CATALYSTS

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The chemistry of cyclic compounds with rings of medium dimensions, containing 8–12 carbon atoms in the molecule, has developed considerably in recent years. The interest in these compounds results from the important part which they played in theoretical organic chemistry, due to a number of unique features characteristic of this class of compound. These features include the unique geometric shape of the molecule and the consequent possibility of interaction between atoms of the same molecule, not directly joined to one another. This interaction in medium-sized rings may take place through the ring (transannular interaction) and may be produced between hydrogen atoms attached to neighbouring carbon atoms (vicinal interaction). Both of these factors lead to an increased energy content in medium-sized rings; this has been called "non-classical" conformational strain and is responsible for a number of characteristic features in the chemical and physical properties.

Transannular reactions not only are characteristic of functional derivatives of medium-sized rings but also take place in the catalytic transformation of hydrocarbons with rings of medium dimensions over hydrogenation–dehydrogenation catalysts. In 1955, Prelog and coworkers [1] observed for the first time the transformation of hydrocarbons containing 9–18 carbon atoms in the ring, over a palladium catalyst at 400°C. Depending on the number of