FIFTY YEARS OF SOVIET PHYSICAL CHEMISTRY

BY

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Introduction

Half a century—this is quite an epoch not only in the development of science, but in the life of humanity in general. This is particularly true for our country. The change in the social structure brought about by the October Socialist Revolution of 1917 became a natural boundary between pre-revolutionary Russia and the Soviet period. The social changes were reflected in the scope of the development of science, which was based now on new principles. An ever-increasing amount of scientific research, a greater number of scientific institutions and of problems studied are characteristic of the Soviet period. Certainly, pre-revolutionary Russia produced many eminent scientists, including chemists. Suffice it to name Lomonosov, Mendeleev, and Butlerov. More than 200 years ago, Lomonosov created the first chemical laboratory at the Russian Academy of Sciences and carried out the first physico-chemical experiments. His was the suggestion to name as "physical chemistry" the field of science ranging between chemistry and physics. He wrote in 1752: "Physical chemistry is a science explaining on the basis of physical notions and experiments the phenomena occurring in mixed bodies during chemical procedures."

Before the Revolution, physical chemistry was developed mainly in High School Institutions and Universities of Moscow, Petersburg, Kazan', Kiev, Kharkov, and some other Russian cities.

The picture changed drastically immediately after 1917. Scientific centers for research in physical chemistry arose not only in High School Institutions, the number of which increased progressively, but also in industrial research institutes and mainly in the Academy of Sciences of the USSR.

The first special physico-chemical Institute was the Karpov Institute of Physical Chemistry, which started its activities in 1918 as the Central Laboratory of the Chemical Department of the National Economy Council. A. Bach was founder and director of this Institute for almost three decades. In the half a century of its existence the Institute has become widely known for its research on surface phenomena, electrochemistry, structure of matter, kinetics and catalysis, radiation chemistry, high-molecular compounds. Many scientists began their scientific activity at this Institute. At present, Kargin, Medvedev, Petryanov-Sokolov, Kazarnovsky, and Kolotyrkin are working there, and the prewar part of Frumkin's work was carried out mainly in this Institute.

One of the oldest chemical institutes of the Academy of Sciences is the Radium Institute founded in 1918.

Chemical physics, as a trend of scientific research, originated at the Leningrad Physico-Technical Institute founded in 1920 by Yoffe. In 1931 an independent Institute of Chemical Physics with Semenov as permanent director separated from the Physico-Technical Institute. The kinetics of chemical processes, particularly of the chain and free radical reactions, catalysis, theoretical and experimental investigations of combustions and explosions were the main problems studied there. Later on, the scope of the Institute research problems became considerably wider, studies in the chemistry of high-energy particles, nuclear chemistry, the chemistry and physics of compounds of high molecular mass, and also kinetics and the mechanisms of biological processes becoming included in its program. A Soviet school of chemical physicists represented by Semenov, Kondratiev, Zeldovich, Kharitton, Voevodsky, Emanuel, Kovalsky, Roginsky, and Goldansky came into being.

An important center of physical chemistry is the Institute of Physical Chemistry of the Academy of Sciences of the USSR, which originated from the laboratory of Colloid Electrochemistry founded in 1930 by Kistiakovsky. In 1945 it was reorganized into the Institute of Physical Chemistry. The present director is Spitsyn. The research program of the Institute includes surface phenomena, physico-chemical mechanics, thermodynamics and kinetics of sorption processes, the theory of chromatography, problems of corrosion, radiochemistry and radiation chemistry. Spitsyn, Dubinin, Rehbinder, Deryaguin, and Chmutov are working at this Institute.

The Institute of Electrochemistry was founded in 1958 on the basis of the Electrochemistry Department of the Institute of Physical Chemistry with Frumkin as director. Its present program of research includes theory of electrochemical processes, electrochemistry of organic compounds, radiation chemistry, quantum theory of chemical reactions, as well as the problems of physico-chemical hydrodynamics and its application to engineering. Frumkin, Levich, N. Bach, and Kabanov work at this Institute.

Research in physical chemistry in its various aspects is done at practically all chemical institutes of the Academy of Sciences. For instance, the structures and reactivity of various organic compounds are studied at the Institute of Organoelement compounds (director—Nesmeyanov). V. Kazansky, Shuikin, Rubinshtein, and Gonikberg are engaged in the investigation of catalytic conversions of hydrocarbons and in the spectral study of organic compounds at the Institute of Organic Chemistry. For many years, Balandin worked at this Institute.

The Institute of Petrochemical Synthesis, organized by Topchiev in 1958, is engaged in investigation of the physical chemistry of polymers and in working out new principles for chemical processing of petroleum hydrocarbons. It studies also the problems of plasma chemistry. The Institute of General and Inorganic Chemistry, founded by Kurnakov, is the center of physico-chemical analysis. The physico-chemical properties of metals, salts, semiconductors and organic compounds in multiphase systems are studied

there, as well as the structures of various metal complexes, particularly those formed by platinum, transuranium and rare elements.

The Leningrad Institute of High-Molecular Compounds is concerned with investigation of the physico-chemical laws for oriented structures. Electrochemical methods for metal processing and electrocrystallization are worked out in Kazan' at the Institute of Organic and Physical Chemistry (director—B. Arbuzov).

Fourteen republics of the Soviet Union have their own Academies of Sciences with a great number of research institutes, including those of chemistry and physical chemistry. One of the oldest and largest is the Institute of Physical Chemistry of the Ukrainian Academy of Sciences, which was founded in 1927 (director Brodsky). It is engaged in research on the problems of reactivity of free radicals, in mass-spectrometric and isotopic investigations of the mechanisms of various organic reactions, the mechanism of polymer degradation, the kinetics of fast reactions, catalysis, and radiation chemistry.

Physico-chemical investigations on the thermodynamics and kinetics of reactions involving complexes, colloid chemistry, and electrochemistry of molten electrolytes occupy a considerable place in the research conducted at the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences. Electrodeposition of metals is studied at the Lithuanian Academy of Sciences (Matulis), heterogeneous catalysis and theory of acids and bases at the Kazakh Academy of Sciences (Sokolsky, Usanovich), the mechanics of polymers at the Latvian Academy of Sciences, and the structures of inorganic compounds at the Moldavian Academy of Sciences.

The scope of physico-chemical research at Universities and other High School institutions, some 750 in all, has become much wider. The Chemical Department of the Moscow State University carries out research on electrochemistry, photochemistry, chemical kinetics, catalysis, chemical thermodynamics and thermochemistry, adsorption, molecular spectroscopy, colloid chemistry, gas-phase electrochemistry, electronography, and physical chemistry of high-molecular compounds. The Chemical Department of the Leningrad State University is concerned with the problems of ion exchange, thermodynamics of multi-component systems, and electrochemical kinetics. Extensive physico-chemical research is carried out at the Universities of Kiev, Novosibirsk, Odessa, Tomsk, Tartu, Lvov, etc., as well as at the institutes of chemical technology in Moscow, Leningrad and other cities.

The physico-chemical journals published in the Soviet Union are: Journal of Physical Chemistry; Kinetics and Catalysis; Electrochemistry; Chemistry of High Energies; Colloid Journal; Journal of Structural Chemistry; High-Molecular Compounds; Metal Protection; and Journal of Theoretical and Experimental Chemistry. Many papers on physical chemistry are published in the Proceedings of the Academy of Sciences of the USSR (*Doklady*), the Transactions of the Academy of Sciences of the USSR (*Isvestiya*), Chemical Series, etc.

This survey of 50 years' development of physical chemistry in the Soviet Union certainly cannot encompass all directions of research. Scientific activities of the authors are to a certain extent responsible for the choice of the topics considered. We hope, however, that this article will give an idea of some of the most characteristic trends of physical chemistry in the Soviet Union and of its contribution to the world of science.

Chemical Kinetics

Though the first chemists observing chemical phenomena were undoubtedly aware of the fact that chemical reactions develop in time, attempts to describe the route of a chemical reaction by means of mathematical expressions were first made only a little more than a hundred years ago.

Menshutkin, a contemporary of Mendeleev and Butlerov, was one of the Russian pioneers in systematic investigations of the laws governing the development of chemical reactions in time. Beginning with 1877, he published many studies on the rates of chemical processes. Van't Hoff, in deriving his kinetic equations, made wide use of the experimental results obtained by Menshutkin.

The mechanisms of chemical reactions are usually complicated. At the end of the last century, the eminent Russian chemist, A. Bach, convincingly demonstrated the complicated nature, which he defined as the "chemical mechanism," of oxidation reactions. At the same time as Engler (1897), Bach advanced the so-called peroxide theory of slow oxidation. The theory implies that oxidation involves an intermediate step—the formation of peroxide—that exerts a stronger oxidative action than oxygen.

The beginning of the twentieth century was a time of great discoveries in physics, in the structure of atoms and molecules. It became possible to elucidate the mechanism of chemical processes, to understand the nature of elementary acts, and to detect the intermediate forms involved in chemical reactions.

Physics and physical methods have opened up new possibilities that were unknown in the past century. It was certainly not by chance that in 1913–1916 a new concept enriching chemical kinetics arose, namely of an unbranched chain reaction (Bodenstein, Nernst). This discovery stimulated to a great extent the development of chemical kinetics and of the general theory of chain reactions, as well as the investigations of elementary reactions involving free atoms and radicals.

Chain reactions.—Until 1925, the concept of unbranched chain reactions remained, according to Semenov, "an exception among all chemical processes that were still treated in terms of old concepts of direct mono- and bimolecular reactions."

In 1925, at the Leningrad Physico-Technical Institute, the co-workers of Semenov, Khariton and Valta discovered a new and extremely interesting phenomenon. In studying the luminescence of phosphorus vapor in the presence of oxygen at low pressures, they noted that the luminescence appeared not immediately on admission of oxygen to an evacuated vessel, but after a certain critical oxygen pressure had been obtained. It was found that at oxygen pressures lower than the critical value the reaction occurred at an immeasurably low rate and became violent after the attainment of a critical pressure value. The latter resulted in the appearance in the reaction zone of many excited molecules, i.e., of reaction products carrying the reaction heat which had not dissipated due to collisions with other molecules. In passing to the ground state, these molecules emitted light.

Semenov and Shalnikov showed that in a vessel of a large diameter the "critical pressure" value is lower and ignition occurs more readily. Along with the critical pressure, there exists also a certain critical diameter (critical size) of the reaction vessel. The results of experiments with addition of inert gases appeared to be quite unexpected. For instance, in the presence of argon, ignition occurred at pressures lower than the critical value.

Semenov explained these phenomena by assuming that the reaction between oxygen and phosphorus vapor is of a chain nature and that the chains may terminate at the walls due to disappearance of atoms and radicals carrying the chain. Then at low pressures the reaction should be slow as the walls would be more accessible for active particles.

A mechanism was conceived that implied the progressive multiplication of free radicals in the course of a chain reaction and thus its progressive acceleration up to ignition, the so-called chain ignition. Semenov defined these processes as branched chain reactions. When branching dominates over termination, the reaction rate increases progressively with time and follows an exponential law. When chain terminations are predominant over branching, the reaction is steady-state, there is no ignition, and the reaction rate tends to a constant value.

Within the next few years, Semenov, Kovalsky, Ryabinin, Zagulin, Shalnikov, as well as Hinshelwood, Garner and others found that similar phenomena are observed also in the oxidation of sulphur, carbon monoxide, and hydrogen. This showed how abundant were the branched chain reactions.

Semenov found that the system of kinetic equations for many active centers may be reduced to one equation for active centers of a similar nature. Very descriptive expressions for the main features of chain reactions were obtained. The monograph by Semenov, "Chain Reactions," published in 1934, is widely known.

Research carried out by Kondratiev was concerned mainly with intermediate active particles (free atoms and radicals) and with elementary reactions involving these particles. It was discovered, making use of the spectral technique, that free hydroxyl, OH, may attain high (super-equilibrium) concentrations in the course of branched chain oxidation of hydrygen. An intermediate formation of COS in the combustion of CS_2 was established. The CS

radical was detected in mixtures rich in CS_2. Large amounts of sulphur monoxide were found to form in the course of slow oxidation of hydrogen sulphide.

In the sixties, Voevodsky with co-workers detected free atoms of hydrogen and oxygen in ESR spectra of rarified flames. The thermodynamic equilibrium concentrations of H and O atoms were found to be greatly exceeded. The formation of O atoms and SO radicals in the combustion of sulfur was also established by means of the ESR technique.

Semenov investigated some essential features of chain reactions related to possible mutual interaction of active particles (the chain interaction theory). Slow auto-acceleration, observed for many reactions such as oxidation of organic compounds, was explained by Semenov as due to "degenerate" branching. Critical phenomena were observed also for slow auto-accelerated reactions (Sadovnikov; Shantarovich; Emanuel). Certain phenomena observed in the oxidation of hydrocarbons, such as the critical temperature coefficient and the appearance of cool flames, were explained in terms of the chain theory (Neiman; Shtern). Research in the field of homogeneous catalysis as an effective means for control of chain reactions made great progress (Emanuel; Nalbandian; Enikolopov).

Interesting results were obtained in the investigation of the mechanism of organic oxidation in the liquid phase. The general scheme of oxidation was greatly extended and supplemented by a number of new elementary reactions (Emanuel; Denisov; Maizus; Bliumberg). New reactions of chain generation, propagation, and branching were discovered.

It was found that slow chain oxidation of organic compounds in the liquid phase is accompanied by a characteristic chemiluminescence (1959–1966). The relationship between the mechanisms and kinetics of slow processes and chemiluminescence was quantitatively investigated. This luminescence was found to be due to the disproportionation of peroxy radicals (RO_2)—the relation, $I \sim (RO_2)^2$, being valid for the intensity of chemiluminescence in many reactions. The chemiluminescence technique was used in studies of the mechanisms of free radical reactions, for the control of technological processes, and for determination of the elementary constants of alkyl (R) and peroxy radicals (RO_2) recombination.

The determination of inhibitor concentrations, as well as of the rate constants for the interaction reaction between the inhibitor molecules and RO_2, was made possible by the measurement of chemiluminescence observed in inhibited oxidation (Shlyapintokh, Vasiliev).

Investigations of elementary chemical reactions.—The investigation of chain reactions and of the mechanisms of other complex reactions has stimulated extensive research in the USSR in the field of elementary chemical acts. Studies of elementary reactions involving free atoms, ions, and excited particles were started as early as the twenties. In order to find out the nature of photochemical dissociation and the energy states of dissociation products, Terenin, the founder of Soviet photochemistry, developed a special optical technique that permitted one to assess the process by the fluorescence spectra of the photodissociation products. This technique appeared to be effective for establishing the nature of the primary photochemical act, not only in photochemical but also in radiation chemical reactions both in the gas and in the condensed phase.

It was established in investigations of the photochemical reactions of aromatic compounds, including dyes, that in contrast to simple compounds, the primary illumination of an aromatic compound in the quartz ultraviolet or in the visible spectral region results in excitation of the light-absorbing molecule without its dissociation. The molecule thus excited can enter into an addition reaction; for instance, it can react with oxygen.

The phenomenon of more intensive fluorescence of aromatic compounds, as a result of vibrational deactivation due to the collisions of the excited molecules, was discovered (Neporent). It was taken as a basis for the stabilized fluorescence technique for the investigation of excited molecules.

In order to establish a quantitative relation between the structures of reactants and their reactivities, Semenov generalized the results of the measurements of the activation energies and heats of radical reactions and showed that the Polanyi equation for exothermic reactions relating the activation energy to the heat of the reaction is valid for many elementary reactions involving atoms or free radicals (1958).

$$E = 11.5 - 0.25|q|, \quad \text{where}$$

E is the activation energy, and q the heat of the reaction.

The theory of homogeneous radical generation of the type $XY+M \rightarrow X+Y+M$ was studied in detail by Sokolov.

A possible bimolecular generation of radicals of the type $AX+BY \rightarrow X+AB+Y$ was also considered. It occurs when at least one of the broken bonds is not very strong, while one of those formed is of a high energy. The occurrence of such reactions was first shown for acetaldehyde oxidation.

It was found, using the ESR technique, that free radicals $(C_6H_5)_3C$ were formed in the system $LiC_2H_5+(C_6H_5)_3CCl$, which was the first direct proof of the formation of free radicals by the interaction of two saturated molecules (1958).

The bimolecular generation reactions were studied in greatest detail for fluorine (Shilov). The reactions

$$HI + F_2 \rightarrow HF + I^{\cdot} + F^{\cdot}$$

$$C_2H_4 + F_2 \rightarrow F^{\cdot} + C_2H_4F^{\cdot}$$

were found to be possible.

A homogeneous formation of radicals in the liquid phase by the interaction between hydroperoxide and hydrocarbon was observed for *n*-decane and cumene oxidation (1960, 1965). An approximate method for the estimation of steric factors in simple and radical bimolecular reactions was worked out on the basis of the transition state theory and the semiempirical classical colli-

sion method. It was applied to many reactions of radicals with alkanes and alkenes (Stepukhovich).

The possibility of a heterogeneous chain generation in various oxidation reactions was first suggested by Poliakov (1927) and experimentally confirmed by Kovalsky (1947). Making use of the differential calorimetry technique, he showed that at least 96 per cent of the heat released in the reaction between SO_2 and CO, that occurs only in the presence of a catalyst (bauxite), is emitted in the gas phase, rather than at the wall surface. This shows that the bauxite surface yields active centers which induce a reaction in the gas phase. The use of the differential calorimetry technique showed that many homogeneous reactions are initiated at the wall.

The mass-spectrometry technique was applied by Kondratiev as early as the thirties in studying the mechanism of complex chemical processes (detection of active reaction centers, free atoms and radicals). This method was further developed by Talrose and co-workers. A new technique was proposed for the determination of reaction rates in the fast reactions of dissociation of excited molecular ions. It permits measurement of lifetimes as low as 10^{-9} sec. Various decomposition reactions of hydrocarbon ions were studied. Proton affinity values were determined for saturated molecules. A fundamental feature of the gas-phase organic ion-molecular reactions involving hydrogen transfer, namely the absence of an activation energy, was established. This accounts for the importance of the ion-molecular reactions in the chemistry of high-energies, in radiation chemistry, photochemistry, the chemistry of plasma and of high temperatures, and cosmic chemistry. A stable methonium ion, CH^+_5 ,was discovered, and this led to new concepts of the possible valence states of carbon. The ready transition of the kinetic to internal energy of an ion upon collision of polyatomic particles was established for the ion-molecular reactions of charge exchange.

Goldansky considered the general theory of tunnelling in chemical kinetics, at Maxwell and quantum energy distributions of the energies of the interacting molecules (1959). A critical temperature, below which tunnelling becomes more probable than overbarrier (Arrhenius) transitions, was established. Goldansky developed also a new "positronium" method for studying the kinetics of fast chemical reactions in the gas and condensed phases (1959–1964). The rate constants for formation of the hydrogen-like positronium atoms and for their subsequent reactions were determined from the lifetimes of positrons and from the intensity of the long-lived component in annihilation.

Kinetics of polymerization processes.—The immensely increased production of high-molecular mass materials, such as plastics, elastomers, viscose, and synthetic fibres, led to a considerable development of research on the kinetics of polymerization processes. Lebedev (1913) and Shorygin (1924), who were the first to start work on the production of synthetic rubber and artificial fibres, must be considered as pioneers in the Soviet chemistry and chemical kinetics of high-molecular mass compounds. By studying the

kinetics of polymerization of diene and allene compounds, Lebedev established a relation between the structure of monomers and their capacity for polymerization.

This line of research was further developed by Medvedev and his co-workers, starting in the thirties. On the basis of the chain theory, Medvedev established the chemical nature of elementary free radical polymerization and copolymerization processes. Bagdasarian showed that thermal and photopolymerization processes are similar in their radical nature. He investigated the effect of conjugation on reactivity, the polar effects, and the relative reactivity of radicals in polymerization (1959).

The reduction-oxidation initiation of radical chain processes of polymerization, and structure formation and degradation of polymers was studied by Dolgoplosk (1947–1957). The redox systems were found to be powerful sources of radicals at low temperatures down to $-50°$.

Kargin and his school are widely known for their fundamental physicochemical research on polymer properties in the condensed phase and in solutions. An essential contribution was made to the modern concepts of the polymerization mechanism for crystalline monomers. A detailed analysis of the polymerization kinetics upon phase transitions led to the concept of "labile pre-orientations," i.e., of the systems involving ordered monomer molecules capable of a certain mobility, necessary for the relaxation of stresses arising in the formation of polymer chains due to the rearrangement of interatomic distances.

Use of the ESR technique in investigations on the catalytic polymerization of ethylene and other α-olefins was first made for Ziegler catalysts (1961). Later it was applied to many new complex compounds. Catalytic systems soluble in hydrocarbons, e.g., $(C_2H_5)_2TiCl_2$–$Al(CH_3)_2Cl$, were studied. The most important conclusion made was that concerning the free ion mechanism of polymerization initiation (Shilov). The kinetics of radiation-induced solid-phase polymerization, characterized by an abnormally high rate and no activation energy at low temperatures, was studied (Goldansky, Enikolopov). Semenov advanced the hypothesis that energy chains are responsible for polymerization in the solid phase. Polymerization of solid monomers by shock waves was discovered (1965).

Kinetics and mechanism of heterolytic reactions.—Many laboratories were concerned with investigation of the mechanism of heterolytic processes in the liquid phase, the catalytic activity of acids and bases in aqueous and non-aqueous solutions, as well as with the effect of the medium on the mechanism of ionization and the reactivity. Criteria for estimation of the reactivities of substances in bimolecular processes occurring in aqueous solutions of strong acids were proposed. Methods for the determination of the ionization constants of organic compounds were worked out to be used when the routine spectroscopic techniques are inapplicable (Vinnik, 1959–1964).

In order to determine quantitative relationships between the reaction rates and the properties of the medium, many processes that occur in polar

media and involve strong electrophilic agents were investigated. The mechanisms of many reactions involving organic cations were studied. It was shown that the thermodynamic and kinetic behavior of carbonium ions is dependent to a considerable extent on the "coordination solvation" due to the donor-acceptor interaction between the free orbital of carbonium carbon and the electron-donating molecules of the medium (Entelis).

Shatenshtein suggested and substantiated the concept of the protolytic (acid-base) nature of heterolytic hydrogen exchange reactions (1949). It was shown that all reactions of isotope exchange may be divided into two markedly different groups. The first comprises the reactions of practically immediate exchange at any temperature without use of catalysts, such as exchange with acid-base deuterium donors at the N-H, O-H, S-H, Cl-Cl bonds. This was called fast exchange. The second group encompasses the compounds for which exchange is either slow or does not occur at all. Fast exchange is observed for compounds with an X-H bond, the X atom possessing a free pair of electrons. A deuteron or a proton adds to the free pair of electrons with the simultaneous abstraction of a proton from another electron pair (Brodsky).

Syrkin suggested that the elementary acts of many chemical reactions occur via five-, six- and seven-member cycles with a sextet of electrons. The mechanism of reactions of aromatic complexes of metals such as ferrocene and ruthenocene and of π-complexes of some metals of the platinum group was investigated. Oxidation of olefins to carbonyl compounds was realized on this basis, this process being of practical interest as well (1960).

Kinetics of chemical reactions at high pressures.—High pressures were widely utilized in studying radical-chain polymerization in the liquid-phase. The reactions conducted under high pressures permitted the polymerization of compounds that were unable to polymerize under ordinary conditions (Gonikberg, 1956).

A method of adiabatic compression and expansion of gases was proposed for studying the kinetics of fast nonisothermal reactions. It was applied later to a quantitative investigation of processes involving cooling at a rate of 10^6 to 10^7 deg/sec (Riabinin; Markevich, 1952). Synthesis of nitrogen oxides in air mixtures and in mixtures with addition of fuel was studied by means of this method. A new technique of obtaining acetylene by "quenching" hydrocarbon flames was worked out. The concept of critical conditions of quenching of the reaction was extended to the more complex reaction of formaldehyde formation during the oxidation of methane (1954–1958).

The yield of the reaction product in the synthesis of hydrocyanic acid in hydrocarbon-nitrogen mixtures was shown to depend on the cooling conditions. The application of the adiabatic compression technique in the investigation of thermal methane decomposition under markedly nonisothermal conditions permitted one to establish the main kinetic features of this reaction (reaction order, activation energy, and sequence of individual reaction steps).

The theory of combustion and explosions.—One of the achievements of

chemical kinetics was the theory of combustion and explosions, proposed and developed by Semenov and his school. As early as 1928 Semenov differentiated the concepts of chain and thermal explosion.

Chain ignition may occur under practically isothermal conditions without appreciable heating of the mixture. Ignition of a strictly chain nature occurs most readily under low pressures. However, an ignition mechanism of another nature, different in principle, may be conceived as well. This is the so-called thermal explosion or thermal ignition.

When the reaction in the vessel is slow and accompanied by release of heat, the latter is consumed in heating the reaction mixture with a partial escape through the wall. The increase of temperature leads to increase of the reaction rate so that heat cannot be removed through the walls fast enough. The acceleration of the reaction becomes progressive. Under certain conditions the generation of heat may exceed its removal and this will result in explosion of the mixture. Semenov derived the well-known expression relating the density of gases to the ignition temperature. The Semenov expression is

$$\log \frac{P_{\text{expl}}}{T_0} = \frac{A}{T_0} + B$$

Here P_{expl} is the minimum pressure at which the mixture ignites on admission to a vessel with the wall temperature T_0; A is a quantity proportional to the effective activation energy for the reaction; and B is a constant determined by the reaction rate as a function of the concentration of reactants and of the heat release conditions.

Zeldovich is the founder of the modern theory of the normal rate of flame propagation, which was widely used in the analysis of experimental results on the combustion of gas mixtures and explosive vapours (1933–1943). The data on flame propagation rates are used for determination of the rates of very fast reactions in flames at high temperatures of 2000 to 3000°C.

As a result of this research, an essentially complete theory for gas combustion, a modern theory for one of the most important phenomena in combustion, namely for detonation, and a method for calculation of the detonation rates, were developed.

Schelkin, Troshin and others discovered and studied specific combustion regimes. The idea was put forward that the motion of gas induced by the expansion of combustion products, and particularly the resulting gas turbulence, has a decisive effect on the increase in the rate of flame propagation (1939–1963). This idea provided an explanation for the laws governing the transition from slow combustion to detonation in tubes, for the accelerating effect of rough walls in combustion and its transition to detonation, and made possible the discovery of new types of combustion: stationary fast combustion and stationary delayed detonation in rough-walled tubes. Pulsated detonation was discovered and an explanation was given for spin detonation (1945–1963).

The decomposition of many compounds, such as methyl nitrate, nitroglycol, lead azide, calcium and barium azides, as well as the supersensitive nitrogen chloride, was studied. Of great importance was the research on the excitation of detonation in explosives. The detonation caused by ion and electron bombardment was investigated. The mechanism of the phenomenon of impact explosion was elucidated (1936). The formulation of the principle that determines the conditions for steady detonation was of great significance for the whole problem of detonation explosives. Steady detonation is possible only if the time of relaxation in the detonation front is shorter than the time of substance dissipation under the action of the very high pressure that develops in the explosion zone (Khariton, 1959).

The mechanism of combustion of explosives was explained by Belyaev, who showed that combustion occurs in the gas phase after vaporization (1946). Sadovsky carried out experiments on the reflection and collisions of shock waves. Research on the mechanical action of the shock wave in air, on the dependence of the maximum pressure and the shock wave pulse upon the weight of the charge and the distance from the explosion site was carried out. A physical interpretation of the similarity law in explosions was given, and the flow of shock waves past obstacles was proved, which is of importance for the estimation of the effect of shock waves on buildings. The expressions derived for the determination of safe distances from explosion sites are of great practical importance.

Scientific problems related to nonsteady motions in a continuous medium were also treated. The reflection of the shock waves from a free surface was studied. The consideration of nonlinear effects led to qualitatively new results and permitted a theoretical estimation of the effect of a shock wave arising from a submarine explosion. The problem of shock propagation in the soil at small distances from the explosion site was solved (Khristianovich; Kompaneets).

Catalysis

Great attention has always been paid in our country to research in the field of catalysis. Of particular importance in the history of this problem are the contributions made by Zelinsky's school (Balandin; Kazansky; Shuikin and others).

Balandin formulated and developed the multiplet theory of catalysis (1929). He showed that an elementary catalytic reaction is possible only at certain ratios of interatomic distances in reacting molecules and in the crystal lattice of the catalyst (the principle of structural consistency). He explained the importance of such factors as the energies of bonds formed and broken in the course of the reaction, the adsorption potentials, and the heats of reaction (the principle of energy consistency).

Rubinshtein investigated the topochemistry of catalysts, the effect of the phase composition, dispersion, and deformation of crystal lattices on the catalytic properties and texture.

Pisarzhevsky was a pioneer in the application of electron concepts to the theory of heterogeneous catalysis in our country (1923). The electron theory of catalysis was developed by Roginsky who showed that the catalyst electrons take part in redox reactions. This initiated investigation of the semiconducting nature of catalysts. The theory of heterogeneous catalysis on semiconductors was further developed by Roginsky and Volkenshtein, who also discovered new types of redox catalysts (1960).

Roginsky proposed a new technique for conducting catalytic reactions under chromatographic conditions. This technique involves combined catalytic conversion of reacting substances with chromatographic separation of the reaction products. It permits one to attain higher extents of conversion compared to the routine conditions at considerably lower temperatures. Later a technique was proposed for conducting catalytic reactions in a pulsed chromatographic system. Laboratory and semiindustrial tests of catalysts are made considerably shorter by the use of this technique.

An interesting concept is the hypothesis advanced by Semenov and Voevodsky about the importance of adsorbed free radicals in heterogeneous catalysis and the ensuing possibility for the catalytic reactions to follow a chain mechanism.

Investigation of adsorbed radicals became of particular significance in recent years because of the wide application of the ESR technique. It appeared possible in many cases to study the structure and chemical properties of these radicals and to establish their importance for adsorption, catalysis, and radiation catalysis (V. Kazansky).

Research on catalysis is carried out on a wide scale also at the recently founded Institute of Catalysis of the Siberian Department of the Academy of Sciences under the leadership of Boreskov. These studies are devoted both to the theory of catalysis and to the scientific basis of the practical application of catalytic reactions. Great attention is paid by Boreskov and his co-workers to the modelling and optimization of catalytic processes.

The kinetic theory for reactions on nonuniform surfaces was developed by Temkin, who proposed the well-known logarithmic adsorption isotherm (Temkin isotherm). On the basis of this theory, Temkin substantiated the kinetic equations for many industrial catalytic processes, such as conversion of carbon monoxide, gasification of charcoal, oxidation of ammonia and ethylene, and hydration of acetylene and ethylene.

Using the concepts of physico-chemical mechanics, Rehbinder developed the principles for regulation and control of the mechanical strength of catalysts (1964). In particular, it appeared possible to increase the strength of the catalyst for oxidative dehydrogenation of propene and butene. Frost and Topchieva investigated silica-alumina catalysts.

Sokolsky worked out new electrochemical methods for the investigation and control of hydrogenation catalysts and discovered a very interesting phenomenon, that of a marked decrease in the electric conductivity of platinum and nickel catalysts wetted with a solvent upon removal of adsorbed hydrogen.

The development (which began in the nineteen thirties) of the macro-

scopic kinetics of heterogeneous processes, including diffusion kinetics, physico-chemical hydrodynamics, estimation of thermal regimes, and theory of reactions in a suspended layer (Elovich; Levich; Todes; Frank-Kamenetsky), proved to be of great importance for industrial heterogeneous catalysis.

An essential contribution to this field was made by Levich, who proposed the term "physico-chemical hydrodynamics" for the field of science involving problems related to the effect of the motion of liquids and gases on chemical reactions and of physico-chemical factors on the motion of liquids (1952). The theory of convective diffusion and heat transfer in turbulent flow, the theory for the elementary act of liquid extraction and bubbling, and methods for the solution of problems of particle transfer and heat transfer in an immobile and fluidized granular bed were developed.

Of great interest is the problem of homogeneous catalytic synthesis in the presence of organo-metallic complex catalysts, which are widely used in the chemistry of high-molecular mass compounds. The fixation of nitrogen by means of such compounds was found to be possible (Volpin; Shilov).

The Electric Double Layer and Electrochemical Kinetics

Considerable attention has been given in the USSR to investigation of the electric double layer. In the first series of papers (Frumkin and collaborators, 1919–1928) the Lippmann equation of the electrocapillary curve was quantitatively verified and also derived from the Gibbs adsorption equation. It was generally believed at that time that the Lippmann equation was applicable only in cases where the behavior of the system was not affected by adsorption phenomena. The proof of its general applicability and electrocapillary curve measurements in nonaqueous solutions showed that the potential differences at the metal/solution interface can arise in the absence of an exchange of ions between these phases as well, due to the adsorption of ions and dipole molecules, including the solvent molecules. For these reasons, the widely used Nernst "osmotic" theory of the appearance of the electrode potentials had to be rejected and attempts to determine the "absolute" zero of potentials were shown to be futile.

On the basis of the developed thermodynamic theory of electrocapillarity, it became possible to interpret quantitatively the complex form of the electrocapillary curve obtained by Gouy in solutions of surface-active organic substances. In this interpretation the uncovered and covered parts of the surface were considered as being two parallel capacitors and use was made of an adsorption isotherm obtained from the Langmuir isotherm by taking account of the attraction between adsorbed molecules—a suggestion originally proposed for the adsorption of fatty acids at the solution/air interface. This method for comparison of adsorption phenomena at these two interfaces was later widely used.

The application of the electrocapillary curve measurements to thallium amalgams and liquid gallium led to the conclusion that the potential of zero charge is dependent on the metal nature. The potential difference at the

ends of a circuit composed of electrodes at the zero charge potential is similar to the Volta, or contact, potential between metals in vacuum. On the basis of these results, an approximate relation between potential of zero charge and the electron work function was established and it became possible to answer the question facing the electrochemists since Volta's time about the relationship between the potential differences measured in aqueous solutions and the contact potentials.

The determination of the shift of the zero charge potential of mercury, depending on the concentration of the adsorbed anion, showed this shift to be larger than the maximum value possible from the point of view of the Gouy—Stern theory of the electric double layer, the so called Esin-Markov effect (1939). This effect can be interpreted only by taking into consideration the discrete structure of the double layer, first suggested in 1933. Later there appeared many studies in the USSR and USA concerned with development of the theory of the electric double layer, taking into consideration its discrete structure (Esin and Shikhov; Ershler; Grahame; Levich, Kiryanov and Krylov; Macdonald and Barlow).

Further investigations of the electric double layer had to do largely with elaboration of the methods applicable not only to liquid but also to solid metals. If an electrode with a sufficiently developed surface operates as a hydrogen or an oxygen electrode, formation of the electric double layer leads to measurable changes of the solution pH. Thus the zero charge potential of the platinum-hydrogen electrode was determined. The development of the electrochemical theory of adsorption demonstrated that the ability of activated carbon to decompose neutral salts with the adsorption of acid, detected by Bartell and Miller, was due to the presence of adsorbed oxygen, and led to the preparation of "hydrogen" carbon, decomposing neutral salts with the adsorption of alkali (Bruns; Burshtein).

Measurement of the galvanostatic charging curves of platinized electrodes with large surfaces permitted separation of the characteristic hydrogen, double layer, and oxygen regions of the potential. These measurements, carried out in conjunction with determination of the surface charge from the adsorption of the H^+ ion, demonstrated the role of the adsorption of hydrogen and oxygen atoms in the establishment of the potential difference at the platinum electrode/solution interface (Frumkin and Shlygin, 1933–36). From the approximate linear dependence of the surface coverage on the potential observed in the hydrogen region, the logarithmic adsorption isotherm, characteristic of the processes involving a decrease in the energy of adsorption with increase in coverage, was obtained (Temkin, 1938). Later Temkin's isotherm was widely used in electrochemical kinetics.

In the postwar period, due to the use of radioactive tracers, determination of the charge of platinum metals was supplemented by separate measurements of the cation and anion adsorptions (Balashova and Kazarinov). For the first time, specific adsorption of inorganic cations was observed and measured both on platinum and mercury. Finally, it was shown recently that

the thermodynamic theory of the electric double layer, developed earlier for the mercury electrode, could be used with some modifications for platinum metals as well.

The object of another series of investigations was to find the reason for the long-known discrepancies between the capacity value, C, of the Hg-electrode obtained from the electrocapillary curve and that derived by direct measurement, the latter being several times as low as the former. Proskurnin and Frumkin (1935) found this discrepancy to be due to the adsorption on mercury of traces of surface-active substances present as impurities in the solution. This showed for the first time the importance of the purity of the solutions used in electrochemical investigations. The above authors also detected the characteristic peaks on the C, φ-curve (φ—the electrode potential), limiting the region of adsorption of organic substances. Henceforth the differential capacity measurements became a fundamental method for the investigation of adsorption of organic substances on mercury, which contributed to the refinement of the theory developed earlier by Damaskin and shed light on the role of the interaction of the π-electrons with the metal in the process of adsorption of aromatic compounds.

In compliance with Gouy's theory of the diffuse layer, the differential capacity measurements in dilute solutions showed a capacity minimum near the potential of zero charge of mercury (1939), which made possible the determination of the potential of zero charge on solid metals. Due to Leikis (1962–1967), the reliability of the measurements of the C, φ-curves on some solid metals now approaches that for mercury. The most reliable data on the potential of zero charge of solid metals were obtained by the methods of adsorption measurement and determination of the capacity minimum in dilute solutions described above. It is of interest, however, to carry out direct measurements of the electrocapillary curve, or of something equivalent thereto, of a solid body. Rehbinder and Likhtman succeeded in solving this problem and demonstrated that the formation of the electric double layer lowers hardness and favors deformation of the solid body, thus facilitating the formation of microcracks and the emergence of dislocations on the surface. Therefore, the potential dependences of hardness or of the inverse creep rate are in the form of an electrocapillary curve and likewise exhibit the influence of the adsorption of surface-active substances. Recently, Gokhshtein developed an original method of measuring the changes in the electrode/solution interfacial tension under polarization with alternating current passing them to a piezoelectric element.

The scope of investigations of the electric double layer can be increased by extending them to electrolyte melts. By measurement of the electrocapillary curve (Karpachev, Stromberg, Smirnov; Kuznetsov) and of the differential capacity (Ukshe, Bukun; Leikis), the potential of zero charge of a large number of molten metals was determined. The determination of the dependence of the differential capacity on temperature, potential, and the nature of the anion and cation over a wide temperature range showed the structure

of the electric double layer in melts to be essentially different from that in aqueous solutions: namely, the presence of a charge on the metal surface causes an alternating distribution of the charges in the melt with an amplitude which diminishes with the distance from the interface (Ukshe and Bukun; Dogonadse and Chismadzhev).

The existence of the dependence of the interfacial tension on the potential and charge leads to the mobility of the metal drops in the electric field on one hand and impedes the tangential motion of the charged surface on the other. Levich and Frumkin gave a quantitative theory of dynamic electrocapillarity, which has permitted one to predict some new curious phenomena, e.g., the dependence of the rate of fall of mercury drops in the electrolyte solution on their charge. As was first pointed out by Frumkin and Bruns (1935), it is the tangential motion of mercury under the action of potential gradients which is responsible for the polarographic maxima discovered by Heyrovsky. On the basis of the dynamic theory of electrocapillarity, a semi-quantitative theory of these maxima as well as of the maxima of the second kind, due to the mercury flow, which were discovered by Kriukova, was developed later.

A large number of investigations were concerned with the elementary act of charge transfer and with the effect of the electric double layer structure on the rate of the electrode reaction. The first quantitative theory of hydrogen overvoltage, according to which the rate of the electrode process can be determined by the discharge step, was given by Erdey-Gruz and Volmer (1930). Shortly after this, Frumkin showed that by considering the negatively charged electrode surface as a base protonated during the hydrogen ion discharge and applying to this reaction the Brönsted relationship between the protonation rate of weak acid anions and their basicity constant, it is possible to derive the Tafel equation, which is obeyed by the hydrogen ion discharge (1932). This conclusion established a relationship between the laws of the electrode processes and reactions in solutions and formed the basis for the theoretical treatment of the elementary act of discharge by Polanyi and Horiuti.

Taking into consideration the location of the discharging ions within the confines of the electric double layer introduced an important correction into the Tafel equation. If the potential at the point at which the reacting particle is located in the transition state of the reaction is designated by ψ_1, the equation of the slow discharge theory in the general case assumes the form:

$$i = k[A] \exp \frac{F}{RT} [-\alpha(\phi - \psi_1) - n_1\psi_1]$$

where i is the current density, $[A]$ the concentration of the reacting particle in the bulk of the solution, n_1 its charge, and $0 < \alpha < 1$. This equation was first derived for the case of the hydrogen ion discharge (Frumkin, 1933) and permits one to explain the experimentally observed dependence of hydrogen overvoltage on mercury upon the current density and on the acid and neutral salt concentrations (Levina and Zarinsky; Bagotzky and Yablokova). The

investigation by Levina and Zarinsky carried out with a stationary mercury electrode, was the first in electrochemical kinetics to involve a thorough purification of the solution used, which became obligatory later. For an accurate comparison with the results obtained from a dropping mercury electrode, it was necessary to solve the problem of the concentration polarization for the case of an irreversible process on a growing drop under potentiostatic conditions (Meiman; Bagotzky, 1947), which required a more complex mathematical apparatus than that used previously.

The problem of hydrogen overvoltage has been taken up repeatedly. At low enough overvoltage the activation energy of the discharge reaction becomes equal to the thermal effect of the elementary act, which leads to a change in the slope of the polarization curve and of the dependence of the overvoltage on the solution composition. Such processes, termed barrierless processes, were theoretically predicted by Krishtalik (1960) and experimentally observed by him in the cathodic evolution of hydrogen on mercury at low current densities. Determination of the activation energy made it possible to estimate the adsorption energy of an H-atom on mercury (29 kcal). This quantity has been the subject of much controversy in electrochemical literature, beginning with the investigations of Kobozev and Nekrasov (1930), who were the first to point (from different theoretical positions) to the significance of the adsorption energy of an H-atom for determination of the dependence of overvoltage on the metal nature. Another limiting case—the activationless discharge which should occur at sufficiently high overvoltages—has not been realized as yet, although we know of similar bulk processes.

The first study of hydrogen overvoltage in alkaline solutions was carried out with nickel (Levina and Lukovtsev). The problem of the mechanism of hydrogen evolution on Ni still remains, however, a controversial point, but applicability of the concept of the slow electroreduction of water molecules to hydrogen evolution from alkaline solutions was conclusively proved for liquid gallium (Bagotzkaya). Hydrogen evolution on mercury at pH >10 under ultrapure conditions is due to a chemical reaction with water of the amalgam being formed (Korshunov, 1961), as was correctly suggested by Bockris and Watson (1952), although under their experimental conditions hydrogen evolution could proceed by the electrochemical mechanism as well. It is curious that in the case of this reaction a partial reversion should be observed to the concepts prevalent prior to the development of modern electrochemical kinetics.

The first direct determination of the rate of the elementary reaction, $H^+ + e^- \rightarrow H_{ads}$, was based on impedance measurements of a Pt-electrode at varying frequencies (Dolin; Ershler, 1940). This study initiated the use of alternating currents for investigation of the kinetics of electrode processes, which became more extensive after the war (Ershler; Randles). Alternating currents were also used for investigation of the kinetics of adsorption (Melik-Gaikazyan). Recently, Levich and Dogonadse developed a quantum-mechanical theory of the elementary act of the hydrogen ion discharge, calculating the probability of simultaneous proton and electron transfers in the ion-electrode system, and demonstrating the essential importance of the dipole solvent fluctuations for the process. They succeeded in explaining by means of this theory how the coefficient α can retain the value $\frac{1}{2}$ over a wide potential range.

Of primary importance for the development of electrochemical kinetics was the determination by Temkin of the physical significance of the activation energy, calculated from the temperature coefficient of the rate of the electrode process (1948).

The structure of the electric double layer exerts a particularly large influence on the processes of electroreduction of anions. The investigation of this phenomenon was initiated by discovery of the dropping characteristic of the electroreduction of $S_2O_8^{2-}$ on mercury (Kriukova, 1949). This anomaly of the polarization curve, which to the first approximation can be expressed by the equation given above, is due to repulsion of the anion by the negatively charged electrode surface. Later, this anomaly was found to be present in the case of many other anions on various electrodes. The results obtained stimulated the study in other countries of the effect of the electric double layer upon the course of electrochemical reactions (Delahay; Gierst; Koryta). The repulsion of the reacting particle from the electrode surface in the case of anions reduction should create favorable conditions for electron transfers to relatively long distances, which, however, has not been confirmed so far. We might expect that the question of the role of direct electron emission in electrode processes will be finally cleared up by the recently developed theory of photoemission from polarized electrodes (Brodsky and Gurevich, 1967).

The electric double layer affects the kinetics of electrode processes, also determining the conditions of adsorption of organic substances. If the presence of foreign adsorbed molecules hinders the electroreduction process, this effect disappears at the desorption potential (Jofa; Nikolaeva-Fedorovich). Due to this inhibition in certain potential ranges, the process rate can be determined by the rate of penetration of the reacting particle into the adsorbed layer (Loshkarev). If the adsorbed particles themselves participate in the electrode process or catalyze it, e.g., in catalytic hydrogen evolution, the effect of the electric double layer on adsorption leads to the appearance of maxima on the polarization curves or to change of their slope (Mairanovskii; Tedoradse; A. Ershler).

Finally, in the evolution of the electrolysis products as gases, e.g., in the electrolysis of water, the electric double layer, which controls the wetting of the electrode surface and the contact angle, determines the size of the gas bubbles (Kabanov and Frumkin, 1933).

The effect of the electric double layer structure on the kinetics of electrode reactions determines the importance of the potential of zero charge as the quantity characterizing the electrochemical and adsorption behavior of

metals. The importance of the potential of zero charge for the theory of the electroreduction of organic substances was first pointed out by Antropov (1946).

Among the electroreduction reactions, special attention was given to the reduction of O_2. It was shown by Bagotzky that on the Hg-electrode the irreversibility of the first step (the addition of e^- to O_2) disappears upon passing from acid to alkaline solutions. This permitted for the first time determination of the exact value of the standard potential of the O_2–H_2O_2 system (1950). Further development of these studies was connected with the use of the rotating disc electrode, which was one of the practical results that emerged from the general theory of heterogeneous chemical reactions in moving media, developed by Levich (see *Ann. Rev. of Phys. Chem.*, Vol. 18, p. 153). The dependence of the current density on the rpm upon transition from the diffusion to the kinetic limitations makes possible the determination of the reaction order, which fact was used in investigation of the mechanisms of the reduction of Cl_2 and of the oxidation of H_2 on Pt (Tedoradse; Aikazyan). Levich developed the theory of the rotating disc electrode with a ring, suggested by Frumkin and Nekrasov. This system permits a continuous control of the formation of intermediate reaction products, which has found application, particularly in the USSR and USA, in investigation of the role of H_2O_2 in the process of reduction of O_2 on electrodes from platinum metals, this problem being of interest in connection with fuel cells (Nekrasov & Müller). A number of studies were concerned also with the evolution of O_2 and the formation of O_3. The use of O^{18} permitted determination of the contribution of the water molecules, the anions of the solution, and Pt oxides to these processes (Gerovich et al.; Veselovsky; Rakov).

The concepts of electrochemical kinetics were widely used in studies on the theory of passivity and corrosion. The explanation of the regularities in the decomposition of amalgams, discovered by Brönsted and Kane, with the use of the theory of hydrogen overvoltage (Frumkin, 1932), was the first example (together with a similar study by Hammet and Lorch) of the interpretation of a corrosion process as the result of the simultaneous occurrence of two conjugated electrochemical reactions. This point of view was later generalized by Wagner and Traud. In the USSR the theory of the dissolution of metals based on electrochemical kinetics was developed by Durdin, Shultin, Kolotyrkin and others, simultaneously with the classical theory of local elements by Akimov and his school, especially by Tomashov. Ershler (1940) found anodic dissolution of platinum in concentrated HCl to be determined by the interaction with the Cl^- ions. He observed this reaction to be inhibited by the presence on the surface of oxygen in amounts equal to fractions of a monolayer. This investigation formed the basis of what can be called the adsorption theory of passivity and for the first time established the role of adsorption of anions in the process of metals dissolution. These ideas were further developed by Kabanov and Kolotyrkin. Kabanov and Leikis demonstrated the accelerating effect of the adsorption of the OH^- ion on the kinetics

of iron dissolution. Kolotyrkin showed that in the primary act of dissolution of a large number of metals, complexes with adsorbed anions are formed. The adsorption of organic bases and their inhibiting action on the acid corrosion of iron and cobalt increase greatly in the presence of bromine and iodine anions, which impart a negative charge to the surface (Jofa).

The results of studies on mass exchange were also used in the investigation of corrosion, e.g., the rotating disc electrode, in investigation of the kinetics of the dissolution of metals (Durdin). Some interesting results were obtained on examination of the electrochemical properties of metals subjected to a programmed pretreatment in the gas phase at low pressures. Thus, it proved that deposition on the iron surface of small amounts of oxygen, which seem to penetrate under the outer layer of the atoms of the metal lattice, somewhat activates rather than passivates iron (Burshtein). Considering the success of the electrochemical theory of corrosion, it was rather unexpected to find that under certain conditions the dissolution of iron, chromium and manganese in acids proceeds by a chemical mechanism, i.e., without the separation of the cathodic and anodic processes (Kolotyrkin and Florianovich).

We are not in a position here to discuss numerous studies concerned with the solution of practical problems in electrochemistry, but it should be noted that interest in fuel cells stimulated a number of studies which shed light on the operation of porous electrodes (Burshtein; Pshenichnikov; Ksenzhek; Chizmadzhev), the electro-oxidation of organic compounds—alcohols in particular (Petry, Podlovchenko; Bagotzky; Vasiliev)—and other problems. Incidentally, the first calculation of the electrochemical process in a pore was made by Daniel-Bek in 1948. In studies on electro-oxidation, special attention was given to the role and mechanism of chemisorption processes, which was a natural sequel to earlier investigations of hydrogen and oxygen adsorption.

Radiation Chemistry

Fundamental studies in radiation chemistry in the USSR were carried out only after the second World War. New methods and equipment were developed which permitted study of the time characteristics of excited ions in the range of 10^{-8} to 10^{-12} sec. Ionic-molecular reactions in different classes of organic and inorganic compounds, which are one of the main types of radiation-induced reactions of chemical transformations, were discovered and methodically investigated (Talrose; Tunitsky). Of decisive importance for investigation of short-lived intermediate radiolysis products was the application of the ESR method and the development of radiospectrometers, which permitted one to detect and identify free radicals, as well as to study their kinetic characteristics under different conditions, in particular in radiation processes (Voevodsky; Blumenfeld).

An important contribution to the radical diffusion theory of water radiolysis was the calculation of track parameters, i.e., the number of primary

particles and their space distribution, performed on data relative to the final products alone (Biakov; Ershler).

Fundamental regularities in the formation of oxidation products, induced by the action of ionizing radiation on organic systems in the presence of oxygen, were established and the earlier stages of the interaction of free radicals with molecular oxygen detected and investigated (N. Bach; Saraeva).

The radiation-induced polymerization in the solid phase at low temperatures was found to proceed in some systems by an anionic mechanism. The possibility of carrying out polymerization at liquid helium temperatures was demonstrated (Abkin).

The radiation-induced grafting of polymers on various inorganic bases was realized, which permits the development of new types of materials with specific properties. The modification by means of radiation of wood impregnated with monomers was found to hold great practical promise (Karpov; Tsetlin).

Molecular Structure

Research on molecular structure in the Soviet Union has been concerned with the nature of chemical bonds, the structures of molecules, of solids and liquids, the stereochemistry of crystals, the interaction of groups and atoms, and the reflection of these effects in molecules.

Of great importance was the research carried out by Chugaev. Already in prerevolutionary times he started systematic investigations of complex compounds involving platinum metals and some other elements. His pupils, Cherniaev and Grinberg, obtained several hundred complex compounds unknown before and studied their properties and possible applications. Cherniaev established the trans-effect law and generalized the results on the mutual effect of intrasphere substituents in coordination compounds (1926). The trans-effect concept provided theoretical substantiation to many multistep syntheses of complex compounds of a prefixed structure, carrying predetermined information. Grinberg and his co-workers made wide use of radioactive isotopes in investigating the reactivity of complex compounds. Of particular interest are their experiments on the kinetics of ligand exchange with foreign ions in solution.

Structural studies carried out in recent years led to many new concepts concerning the spatial structures of complex ions of various metals. The relative abundance among the transition metals of rather uncommon polyhedrals with five-and seven-fold coordination was established. Polymer structure, accounted for by bridged atoms and groups of atoms such as halogens, oxygen, water molecules, and hydrazine, as well as metal-metal bonds, was observed in many cases, e.g., in complex acetates of uni- and bivalent rhodium and in bivalent rhenium halides. As a result of structural studies combined with other physico-chemical techniques, some new types of chemical bonds, such as the multi-centered bonds in transition metals, multiple bonds

and, particularly, metal-metal bonds, were found and their characteristics established (Zviagintsev; Porai-Koshits; Syrkin; Diatkina).

It is impossible to dwell here on the contribution of Soviet physicists to the theory of solid structure. However, Frenkel's research on crystal-lattice disorder, and the exciton concept he proposed, cannot be left unmentioned.

The investigations of Belov and his school on the crystal chemistry of silicates showed that the silicon/oxygen radicals of the type taken as the basis for the Bragg classification represent but a part of the many "bricks" of which the silicates are built Di-ortho groups (Si_2O_7) forming chains, bands, and rings of a geometry very different from that of similar constituents in the elementary Bragg "bricks" should also be considered basic to the chemistry of crystal silicates. The main reason for the transition to a new structural unit is the presence of large cations (Ca, Na) instead of the smaller ones such as Mg, Fe, Al, which played a leading role in the Bragg structure of silicates. Belov's research led to the seemingly paradoxical conclusion that cations, rather than the silicon/oxygen radicals, form the structural base of silicates. Strong, but not rigid, readily deformable silicon/oxygen radicals accommodate themselves to the various structural arrangements of cations.

Starting in 1944, investigations on the packing of molecules in crystals of organic compounds were carried out by Kitaigorodsky. The concept of a dense molecular packing, the determination of structure on this basis, the so-called geometrical analysis, and the symmetry laws which follow from the main law of packing have been used for investigation of low-molecular mass compounds as well as for high polymers.

The discovery of molecular light scattering, made by the Soviet physicists Mandelshtam and Landsberg, simultaneously with the Indian physicist Raman, was of extreme importance for the development of the theory of molecular structure. The light-scattering technique was widely used in our country, particularly in the investigation of hydrocarbons.

In 1944, Zavoisky discovered the phenomenon of electron spin resonance. The discovery of nuclear magnetic resonance by Purcell and Bloch followed in 1946. The investigation of ESR, NMR, and also of some other related phenomena led to a new powerful method for the determination of molecular structure—that of chemical radiospectroscopy. We owe to Voevodsky the wide use of this method in our country. Since 1953, radiospectroscopic studies of the properties and reactions of free radicals have become one of the main trends in his scientific activities. By means of the ESR technique, he succeeded in establishing the structures of active centers of oxide catalysts and later elucidated the mechanism of their interaction with molecules reacting at the catalyst surface.

Goldansky is presently engaged in application of the Mössbauer effect (gamma-resonance spectroscopy) in various fields of chemistry. He was the first to observe the Mössbauer effect in polymer and amorphous substances. The differentiation of the role of adjacent and remote chemical bonds in gammaresonance spectra became possible. The asymmetry of quadrupole

splitting in gamma-resonance spectra of polycrystals, known in the Western literature as the Goldansky effect, was observed and investigated quantitatively. The structures of many complex and organo-element tin and iron compounds were studied.

Wide use of ESR, NMR, NQR and other methods as well as of physicochemical techniques led to great advances in investigations of the reactivity of chemical compounds, particularly in the treatment of such important theoretical problems of organic chemistry as conjugation, dual reactivity and tautomerism (Kabachnik), aromaticity, formation of π-complexes (Kursanov), etc. New concepts of weak interaction and of noncoplanar conjugated systems were developed. The features of atomic interactions in sandwich compounds, particularly in the series of ferrocene derivatives, were established (Nesmeyanov). Mechanisms of the substitution reactions for saturated and unsaturated carbon atoms were elucidated. Conjugation in polyfluororganic compounds was investigated and permitted establishment of some new intramolecular rearrangements (Knuniants).

Quantum Chemistry

Among the studies in quantum chemistry carried out in the Soviet Union, those by Fock (1930)—one of the authors of the well-known Hartree-Fock method—should be considered first, since they are of fundamental importance for all multi-electron atomic-molecular problems. Fock combined Hartree's method of the self-consistent field with the variation principle for choice of the optimum form of electron orbitals, making an allowance for the first time for electron exchange effects. Independently of Fock, Slater also gave a determinant version of the wave function of a many-electron system.

In quantum chemistry the Hartree-Fock method forms the basis of the molecular orbitals method, which is in general use now. Essentially, this method can be considered as an application of Fock's general approach to the case of molecules.

On the basis of a reasonably "roughened" version of the Hartree-Fock method, Rutan suggested a procedure for determining molecular orbitals which is widely used in numerical calculations of the electronic structure of small molecules. It should be noted that Rutan's method of varying only a small number of parameters in postulating the general form of electronic functions was earlier suggested and used by Fock (1931).

In the Hartree-Fock method no allowance is made for the electronic correlation effects, which is necessary for the results obtained to be in agreement with experiment. The basic ideas of taking account of these correlations were considered by some Soviet authors. First of all, we should mention the so-called configuration interaction method, in which the wave function is taken as a linear combination of different determinants corresponding to different configurations. This method was proposed by Hartree and Swirls, as well as by the Soviet physicist Yutsis (1931), and was developed later by his school.

Another method of taking account of the correlation, referred to as the method of an incomplete separation of variables, began to develop as the result of studies by Fock, Petrashen and Veselov. Essentially, it was suggested in these studies that in plotting the wave function, the pair functions depending on the coordinates of two electrons should be used along with the one-electron function. In subsequent studies by the same authors (1940–1941) the method of incomplete separation of variables was applied to the calculation of some particular atoms. In recent years the above method was rediscovered by Sinanoglu.

Side by side with the molecular orbital method, the method of valence bonds was widely used, especially in the thirties. At present, this method has been largely discarded, although such outstanding scientists as Heitler, Born and Weil contributed to its development. A considerable contribution to the development and refinement of this method was also made in our country by Rumer and Hellmann (1937). A very attractive concept of the spin-valence was advanced and a special mathematical apparatus of invariants developed. In particular, Rumer formulated a very convenient rule for finding the spin-invariants of polyatomic molecules, which is now known as the Rumer rule. Although so far the method of valence bonds has not come up to expectations, it is still to be hoped that it will contribute to further progress in quantum chemistry.

Recent theoretical studies by Tolmachev (1962) deserve special notice. Tolmachev applied the methods of the quantum field theory and, in particular, that of Feynman diagrams and the apparatus of Green's functions to the atomic-molecular functions. The application of the apparatus of field theory led to generalization of the molecular orbital and valence bond methods.

Soviet scientists also carried out a number of investigations on the use of the molecular orbital method and on the interpretation of the structure of more complex molecules. The best known are those by Syrkin and Diatkina and their collaborators, as well as those by Bochvar and Veselov. Below are some of the results obtained, given as an example only. Calculations carried out by Diatkina and collaborators for oxyanions of transition metals, such as permanganate and chromate, showed that the charge of the central atom in these molecules is much less than the value to be expected from electrostatic concepts and is equal only to $+0.5$ to $+1$ of the elementary charge. The calculations of the valence states of noble gases led to the conclusion that the valence excitation due to the promotion of one of the paired electrons to higher levels requires a very high energy and cannot cause a chemical bond to be formed, even in the case of xenon. This is an important argument in favor of the interpretation of the bonds in the noble gas compounds on the basis of the concepts of delocalized molecular orbits.

Liquid State Theory, Solutions

Frenkel was the first to apply consistently the general ideas of statistical physics to the investigation of the liquid state (1946). He advanced the concept of the jumping mechanism for the thermal motion of liquid molecules. This idea led to the understanding of a number of specific features of the liquid state, particularly the mechanism of transfer processes. Bogoliubov (1946–1965) developed a general approach to the calculation of thermody-

namic properties of one- and multicomponent systems based on studies of the molecular functions of the particle group distribution (the Bogoliubov-Born-Green-Ivon method). The correlation-functions method, which found wide use both in the USSR and in other countries, proved to be especially helpful in the consideration of the short-range order in liquids. It was by this method as well as from some natural assumptions that the short-range order in simple liquids was calculated. The equations of state and the thermodynamic functions both of simple liquids and of strong electrolyte solutions were found. Danilov and his pupils carried out some fundamental studies on determination of the structure of pure liquids and solutions. The developed method for an integral analysis of the curves of the intensity of scattering of monochromatic X-ray radiation showed the presence in liquids of a short-range order, similar to that in crystals.

A number of important results on the theory of electrolyte solutions were obtained. Semenchenko was the first to advance the concept of ion-pairs formation in electrolyte solutions and to give a physical picture of this phenomenon and its simplified mathematical description (1924). Somewhat later a similar concept was suggested independently by Bjerrum (1926). The mathematical development of this concept is still continuing. Using Bogoliubov's method of correlation functions, Tiablikov and Tolmachev showed that a consistent statistical approach to the calculation of the free energy of an electrolyte solution gives automatically a correction for the ion-pairs formation. Levich and Kiryanov used Bogoliubov's method in the derivation of the most general expression for the free energy of an electrolyte solution; for this purpose they substituted at small distances an arbitrary unknown potential for the coulomb potential. Depending on the potential function chosen, the obtained expression can describe a purely coulombic interaction, taking into consideration the ion-pair effect. In the case of a non-coulombic potential of the short-range action, this expression takes account of the Brönsted-Guggenheim effect of "specific" ion interaction.

A considerable contribution was also made to the development of the thermodynamics of ion solvation. On the basis of the concept that the values of the ion solvation energy in different solvents become closer with increasing ion radius, V. Pleskov showed that, using an electrode reversible with respect to cesium or rubidium ions, it is possible to compare the chemical solvation energies of other ions in different solvents. Pleskov's ideas were later developed further by Strehlow in Göttingen. Izmailov suggested a method for division of the total energy of hydration into ionic components, consisting in extrapolation of the sums and differences between the solvation energies of a particular ion and some other ions with an ever-increasing radius to the infinite radius of the latter (1958). Samoilov drew a picture of the structure of aqueous solutions, considering hydration as the influence of ions on the translation motion of the neighboring molecules rather than as the binding of water molecules. His concept of positive and negative hydration based on the above picture was confirmed by the results of NMR measurements.

A very important, but probably yet not fully appreciated, series of investigations on the mobilities of ions, with the use of a refined form of the moving boundary method, has been carried out during recent years by Konstantinov and his collaborators. They succeeded in working out a practical method of quantitative determination of microamounts of cations and anions, the only requirement being the existence of a minute difference in the mobilities of ions. The method for the first time made possible an electrochemical separation of amino acid ions. Conclusions concerning the hydration of ions have been drawn.

Detailed investigations of the physico-chemical properties of nonaqueous solutions, especially in liquefied gases (ammonia, hydrogen halides, sulfur dioxide) and of the isotopic hydrogen exchange reactions in them, carried out by Shatenshtein and collaborators, affected significantly the development of the theory of acids and bases. The conventional concept of acid was extended to include hydrocarbons, and a method was suggested for the determination of acid strength of hydrocarbons by measurement of the kinetics of isotopic hydrogen exchange.

Surface Phenomena and Disperse Systems

The investigation of phenomena at interfaces has been a traditional subject of research in Russia. Thus, Langmuir's well-known papers published in 1916–1917 were to a considerable degree based on the investigations of two Russian scientists: Gurvich's—on the chemical nature of adsorption forces as the manifestation of secondary valences—and Shishkovsky's—on the dependence of the decrease in the surface tension of water caused by fatty acids upon their concentration. In the very first years of the Soviet period Frumkin suggested a general equation of state of the substance in the adsorption layer. Later he investigated the phenomena of thermodynamic instability of wetting films and their rupture upon adhesion of a gas bubble to the surface of mercury or of a solid in an aqueous solution, involving the formation of a finite contact angle and of a polymolecular residual interlayer ("the surface liquid phase") at the boundary with the adhering bubble. These concepts were used to explain the elementary step of flotation processes and formed the basis of some relevant investigations of Soviet scientists (Eigeles; Klassen; Bogdanov).

Deriaguin developed the first quantitative theory of coagulation of disperse systems by electrolytes. His studies were developed further in Holland, USA, Bulgaria, and England and led, in particular, to a direct theoretical calculation of the kinetics of spontaneous thinning of two-sided liquid films (Sheludko). By direct measurement of the forces between solid surfaces at relatively large distances, of the order of tenths of a micron, Deriaguin could for the first time determine directly the van der Waals' attraction and experimentally verify Lifshits' theory of molecular long-range interaction, which takes account of the electromagnetic lag. Using some original methods, he showed that the effect of a lyophilic surface on the structure of a liquid can extend to the depth of many tens and even hundreds

of molecules. Deriaguin and collaborators found that in thin capillaries the anomaly of the temperature dependence of water density observed below 4°C disappears. Recently, some quite unexpected properties of water obtained through condensation of water vapours on a quartz surface under definite conditions were observed. Deriaguin and Krotova discovered new electrical phenomena associated with adhesion detachment and established the importance of electrical factors for adhesion.

A new trend of research was advanced and developed by Rehbinder and collaborators. In 1928 he showed that reversible adsorption from the surrounding medium on the surface of solids (crystals, glasses) can decrease considerably the mechanical strength or reduce the resistance to deformation. As the result of investigations in the USSR as well as in the USA and other countries, this phenomenon is now widely known as the "Rehbinder effect." It is due to the decrease in the free surface energy—the work of formation of new surfaces of a solid *in statu nascendi*—which was proved by direct surface tension measurements of a thin metal foil by the "zero creep" method at elevated temperatures (Likhtman). Adsorption greatly increases the probability of the formation of new surfaces (in microcracks) of deformed solids starting from various structure flaws. These phenomena are of a kinetic nature: the adsorption layers must spread (by the mechanism of two-dimensional migration) within the time of the development of new surfaces, which is determined by the deformation rate or time of loading. Depending on the magnitude of the interfacial energy decrease, the stressed state conditions and temperature, the adsorption effects can assume any form to the extent of a practically complete loss of strength (in the case of spontaneous dispersion of solid bodies into mosaic blocks in a strongly surface-active medium). The adsorption effects due to liquid surface-active metals in the form of thin coatings cause brittleness in highly plastic bodies—even single-crystal metals (Likhtman, Shchukin). On the basis of the dislocation concepts, Shchukin developed a quantitative theory of the decrease of strength and plastification of crystals due to adsorption.

These effects are increasingly utilized in practice in the drilling of rocks, in the fine dispersion of solids, and in the pressure treatment and cutting of metals, as well as for improving the action of lubricants, and in wear prevention. They might also be helpful in increasing the strength of materials under operating conditions, which can be achieved primarily by elimination of all detrimental surface-active media and impurities.

Rehbinder's investigations have made an important contribution to the development of modern colloid chemistry as the science of surface phenomena in disperse systems. Rheological studies of structured dispersions (Rehbinder; Segalova; Serb-Serbina) showed that they can be divided into two large classes—the thixotropic coagulation structures, which reversibly recover after breaking, and irreversible condensation (crystallization) structures, formed (e.g., in setting of cements) by intergrowth of the particles of the nascent new phase or by interlacing. The relatively low strength, the plasticity, and the high elastic properties of the coagulation structures are always associated with residual thin interlayers of the liquid medium between the contacting particles.

The investigations of disperse structures led to the development of methods for the production of high-strength, durable, finely dispersed materials (concretes, ceramics, metal ceramics). Together with studies on the surface phenomena in solid bodies, these investigations form a new field of chemical science—the physico-chemical mechanics of materials.

Extensive investigations on gas adsorption and the structure of adsorbents—activated carbons, silica gels and zeolites—were carried out by Dubinin and his co-workers, who developed methods of oriented synthesis of these adsorbents. The statistical theory of adsorption on heterogeneous surfaces was developed by Temkin, Roginsky, and Zeldovich. Kiselev performed precision measurements of the heats of adsorption, which were compared with the results of quantum-mechanical calculations. Terenin was the first to use spectroscopic techniques for the investigation of surface compounds and adsorption processes.

Chromatographic analysis is known to have been proposed by the Russian botanist Tsvet in 1903. In recent years a number of fundamental investigations on the theory and new methods of chromatography were carried out in the USSR (Todes; Gapon; Bressler; Fuchs). Of particular importance are the methods of thermo-chromatographic analysis of gas mixtures (Zhukhovitsky, Turkeltaub).

A number of important problems in the field of aerosols was solved. The conditions for the formation and precipitation of fogs, control of these processes in the atmosphere, removal of airborne particles from gases, and charging and discharging of these particles were established (Fuchs; Petrianov-Sokolov; Deriaguin and Dukhin; Amelin).

Physico-Chemical Analysis; Equilibria in Multiphase Systems

The name "physico-chemical analysis" was suggested in 1913 by Kurnakov for the field of chemistry concerned with the investigation by means of various physico-chemical methods of transformations in chemical equilibrium systems and of their geometric representation. In the Soviet period great progress has been made in this direction by Kurnakov and his school. One of the main methods used in these investigations is the graphic representation of the experimentally determined relationship between the composition and some property of the system in the form of "composition-property" diagrams. The analysis of these diagrams permits one to assess the nature of the interaction between the components of the system as well as the nature and limits of existence of phases, which can be individual compounds or solid and liquid solutions.

An example of this approach is the discovery made by Kurnakov at the beginning of the twentieth century of compounds with varying composition which have no singular points on the "composition-property" curves. These compounds he called "berthollides" and defined as phases formed by com-

pounds dissociated both in solid and liquid states. The true composition of a berthollide lies beyond the phase, in contrast to "daltonide" phases, which have a singular point within the limits of the "composition property" curve.

The application of the concepts of crystal chemistry (Boky, 1956) permitted representation of the process of formation of a berthollide as an incomplete incorporation (due to unfavorable thermodynamic conditions) of the atoms of the second component, occupying a different Fedorov regular system of points than the first component. For this reason the phase cannot attain the limiting constant composition. By extrapolating the process to total filling of the regular system of points, it is possible to find this composition.

In recent years, physico-chemical analysis was extended to include new areas of investigation, e.g., phase equilibria in multi-component aqueous salt and alkaline systems at high temperature and pressures. Special equipment and methods were developed for the determination of solubility at melt-solution interfaces at 600 to 650° and 300 to 350 atm (Ravich).

During recent years, investigations of complex water-salt systems, started by Kurnakov and Zhemchuzhny as early as the beginning of the twentieth century, were completed by plotting the total polytherm of the quinary system of sodium, magnesium and potassium sulfates and chlorides from complete freezing to 100° (Lepeshkov; Yanatieva; Bergman). The investigations by Kurnakov and his school in the field of water-salt systems played an important part in industrial exploitation of natural salt deposits in our country.

Extensive investigations of complex systems based on iron, aluminium, and different rare metals led to the appearance of new heat- and corrosion-resistant alloys (Grigoryev; Kornilov).

With the ever-increasing complexity of multicomponent systems to be investigated, the methods and constructions of multidimensional geometry were resorted to (Radishchev; Perelman) and further progress was made in the topology and metrics of chemical diagrams (Stepanov; Anosov). Refinement of the thermal analysis methods led to the elaboration of precision termography, which made possible express phase analysis with microweights of hundredths of a gram (Berg; Tsurinov).

Soviet science made another essential contribution to the problem of equilibria in multiphase systems through the studies of Krichevsky.

Until recently, the concept of unlimited mutual solubility of gases was a dogma, although in 1894 van der Waals pointed to the possibility of gas-gas equilibria. His hypothesis was first proved in 1941 for the ammonia-nitrogen system. The experimentally confirmed existence of the gas-gas equilibrium (now for over 30 systems) permitted a comprehensive picture from the multitude of data on the liquid-gas equilibrium. In 1926 Konstamm posed the question as to the existence of critical phenomena of a higher order with more than two co-existing phases becoming identical. In 1963 this critical point of a higher order was experimentally found in the water-butane-acetic acid system with the three phases becoming identical simultaneously.