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WORK OF THE INSTITUTE OF PHYSICAL CHEMISTRY IMENI L. V. PISARZHEVSKIY, ACADEMY OF SCIENCES UKRAINIAN SSR

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The research chair of electronic chemistry, which was organized by L. V. Pisarzhevskiy at Dnepropetrovsk in 1922, expanded rapidly. In 1927 this chair was transformed into the Institute of Physical Chemistry, which was included in 1936 into the organization of the Academy of Sciences Ukrainian SSR, and was named after its founder in 1938. The Institute of Physical Chemistry imeni Pisarzhevskiy was the first chemical research institution in the Ukraine and the first physicochemical institute in the USSR.

During its whole existence the institute has worked in close collaboration with the scientific institutions of the other Union republics, primarily the institutes of the Academy of Sciences USSR. For a number of years the institute was the principal center of the development and dissemination of the new electronic theories in chemistry, which have now been firmly inculcated into Soviet science. More than 800 publications, most of them contributions to All-Union scientific periodicals, have originated at the institute. The institute has also published a number of monographs and textbooks. A series of meetings and All-Union conferences of physical chemistry, in which the most prominent Soviet chemists participated, were held at the institute. Currently the institute maintains close contacts with a number of USSR scientific institutions and conducts investigations in collaboration with some of them.

The scientific basis of the Institute of Physical Chemistry was formed by the important chemical school created by L. V. Pisarzhevskiy, who in 1914 explained the fundamental chemical processes, problems of valency, various aspects of the structure of chemical compounds, and other chemical phenomena from the standpoint of electronic concepts. Subsequently, Pisarzhevskiy and members of his group further developed the electronic theory. On the basis of this theory they explained redox processes, processes which take place in electrical batteries, and the structure of many organic and inorganic compounds. Pisarzhevskiy's successors are continuing to work along these lines at the Institute of Physical Chemistry imeni Pisarzhevskiy, which has become one of the basic physicochemical institutions of the USSR.

Brief reviews of the work done by the institute in various fields follow.

Work in Theoretical and Applied Electrochemistry

Until the end of the nineteen thirties, electrochemistry occupied an important place in the work of the institute.

To investigate the state of electrolytes in solution, A. I. Brodskiy and his collaborators (N. S. Filippova, Zh. M. Shershever, L. V. Korchagin, A. M. Zak, F. I. Trakhtenberg, and others) applied optical and electrochemical methods between 1927 and 1934. An interferometric method was developed at the institute by means of which the ionic refractions in very dilute solutions could be measured directly. It was found that these refractions are additive in the case of strong electrolytes, i.e., that strong electrolytes are dissociated completely in very dilute solutions. This disproved the results of Fajans, who measured refractions in concentrated solutions and found on extrapolation to high dilutions that the refractions in the case of strong electrolytes were not additive. Fajans concluded that dissociation of strong electrolytes in dilute solutions is not complete. In other work done at the institute, Raman spectra were used to determine the degree of association of ions and molecules in solution. In mixtures of trichlorides of the elements of the 5th group, no association products were found. On the other hand, there was displacement of frequencies

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brought about by the interaction of polar solvents with the dipols formed by the molecules of the dissolved trichlorides. In a series of investigations the applicability of the Debye-Hueckel theory under various conditions was critically examined and its validity for nonaqueous solutions proved in a number of cases.

A. I. Brodskiy's theory of the dependence of electrode potentials and equilibrium constants of ionic reactions on the nature of the solvent was checked on mercury and quinhydrone circuits and found applicable. A general theory of quinhydrone and quinone-hydroquinone electrodes was developed and found in agreement with experimental data. More precise values of the solubility products of a number of mercurous salts were obtained. The diatomic structure of the mercuro-ion was definitely proven. The formula which establishes the linear dependence of electrode potentials and of the equilibrium constant on the inverse value of the dielectric constant of the solvent, and which expresses a relationship that had been derived earlier in a simplified manner on the basis of the theory mentioned above, was proven in a more rigorous fashion under consideration of the diffuse structure of the double electric layer. This formula was later also obtained by Bjerrum and usually bears his name. It has been applied frequently since then in research on the following subjects: the dependence between the nature of the solvent and the chemical activities of the solutes, the strength of acids and bases, the equilibrium constants of ionic reactions and tautomeric transformations, electrode potentials, polarographic curves, etc.

The work on the thermodynamics of solutions that was carried out at the institute was a continuation of research on the subject done by Pisarzhevskiy.

Between 1939 and 1941 I. G. Ryss studied the thermodynamics of complex compounds of fluorine with boron and silicon in solutions. Particular attention was paid to the equilibria of hexafluorosilicates and to the kinetics of their decomposition.

A second line of electrochemical research, which was pursued by a group of workers headed by V. A. Royter and in which V. A. Yuz and others participated, dealt with the study of nonequilibrium electrode processes. The theory of the delayed discharge of hydrogen ions, which had been developed by a number of investigators, could not be applied without difficulty to the discharge of metal ions. A new oscillographic method was applied at the institute. The interpretation of the oscilograms and of the kinetic curves led to the conclusion that the fundamental mechanism of the processes taking place at metal electrodes is identical with that of processes taking place at the hydrogen electrode.

It was further concluded that the specific effects taking place in connection with the formation or destruction of the crystal lattice of metals occur because of the differences in the work of activation produced by differences in the degree of orderly arrangement within individual crystal surface areas. The work in question furnished the basis for the formulation of a unified theory of electrode processes that applies both to gas electrodes and metal electrodes. The contradictory results obtained in former work were caused by inaccuracies for which inadequate consideration of changes in the surface area of the electrodes and of differences in the activity of the electrodes at different current densities was responsible. A method was developed which made it possible to measure the changes involved and by taking them into consideration determine experimentally the value of specific velocities of the discharge of ions and the formation of ions at electrodes under equilibrium conditions.

Evaluation of the results obtained made it possible to bring further precision into the determination of the role which microfactors and macrofactors play in the electrodeposition of metals and their electrolytic dissolution.

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In the field of applied electrochemistry work was done principally on corrosion. During 1938-1941, A. S. Afanas'yev subjected to critical study the methods used in the laboratory determination of the corrosion stability of iron and proposed new, improved methods. Furthermore, the electrochemical processes involved in corrosion were investigated and improved methods were proposed for the pickling of Cromansil [chromium-manganese-silicon steel] pipes and wire at metallurgical plants (A. S. Fomenko, I. S. Novosel'skiy, and others).

Before World War II the work done by the institute in the field of the electrochemistry of solutions represented a major portion of work done in this field in the USSR. Both All-Union physicochemical conferences devoted to electrochemistry (the 5th in 1929 and the 12th in 1935) were held at the institute. The first conference dealt principally with the state of dissolved electrolytes, while the second was devoted to the interaction of dissolved substances with the solvents and the effects which these substances have on the properties of the solutions.

Work on Catalysis and Adsorption

Work in the field of catalysis has been one of the principal activities of the institute since its foundation.

Between 1924 and 1938 Pisarzhevskiy and his collaborators created the electronic theory of catalysis, according to which interaction between two different species of molecules at a catalyst which exhibits metal conductivity takes place through the interaction of molecules of one of the two species with the free electrons, so that active radicals are formed. In addition to considering chemical properties, Pisarzhevskiy's theory pays considerable attention to the following properties of catalysts: electrical conductivity, parameters of the crystal lattice, presence of uncompleted electron shells in the atoms of the catalyst, and the work performed to bring about the escape of an electron. The possibility that light may affect adsorption and catalysis is also taken into consideration by this theory.

At the time when Pisarzhevskiy proposed his theory of catalysis, this theory was far in advance of the contemporary state of knowledge. Only in recent years has the electronic theory of heterogeneous catalysis been revived through the work of S. Z. Roginskiy, a former pupil of Pisarzhevskiy who is head of the foremost school of catalysis in the USSR, and F. F. Vol'kenshteyn. Their views on the nature of catalysis are close to those held by N. N. Semenov and others.

The concepts of Pisarzhevskiy's theory were checked on two model reactions: the formation of water from hydrogen and oxygen, and the decomposition of hydrogen peroxide.

At Pisarzhevskiy's initiative, work on the kinetics and mechanism of other catalytic reactions was started at the institute in 1933. The work done by V. A. Royter and his collaborators (M. T. Rusov, M. Ya. Rubanik, I. A. Khrizman, G. P. Korneychuk, and others) in this field was particularly prolific: this group investigated the synthesis and decomposition of ammonia, the conversion of carbon monoxide, the selective oxidation of hydrogen sulfide, the oxidation of carbon monoxide, of acetylene, and of sulfur dioxide, the incomplete oxidation of olefins and of naphthalene, etc. In addition to the kinetics of processes involved in catalysis, the adsorption of the reacting gases and the mechanism of catalysis were studied. In research on the adsorption of hydrogen and nitrogen at iron catalysts and iron-ammonia catalysts, it was established that the rate of the activated adsorption of nitrogen at the catalyst is equal to the rate of synthesis of ammonia, i.e., the rate of the adsorption of nitrogen determines the over-all velocity of the process. New methods for determining the surface area of ammonia catalysts and their permeability to gases were developed. Ways were found for eliminating harmful side reactions which occur in the catalytic oxidation of hydrogen sulfide in the presence of hydrogen.

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The most important result of the series of investigations outlined above was clarification of the important role that transfer phenomena play in the action of porous industrial catalysts. The fact was demonstrated that the influence of transfer phenomena had been underestimated before, and methods were developed which made it possible to determine experimentally the effect produced by these phenomena. As a result, a theory of the kinetics of processes taking place at porous catalysts was developed. Application of this theory to the processes under investigation led to improvements in the efficiency and selectivity of industrial catalysts. In the course of this work, the true kinetics of the catalytic processes in question, which are usually obscured by macrokinetic factors, were elucidated. The processes of ammonia catalysis were investigated in particular detail.

Many of the results obtained in theoretical investigations of this type were applied in industrial work. The research done by the institute has contributed in a considerable measure to the fact that macrofactors are considered widely in work on catalytic phenomena done by Soviet specialists in this field.

For the first time, the idea that intermediate compounds are formed in the course of oxidative catalytic processes that take place in the presence of metal oxides was subjected to a direct experimental check (F. M. Vaynshteya and G. Ya. Turovskiy). It was shown that during the catalytic oxidation of carbon monoxide with oxygen in the presence of copper oxide, or manganese dioxide, there is no exchange between the oxygen of the metal oxides and the oxygen of the gas phase. This refuted the widely held view that there is alternate reduction and oxidation of the catalyst during catalysis.

Another line of research on catalysis which received considerable development at the institute pertains to heterogeneous-homogeneous catalysis. The most important result of the research activities in this field, which are headed by M. V. Polyakov, has been creation of an experimental basis for the theory of heterogeneous-homogeneous catalysis, i.e., a theory which united into one system chain-radical and catalytic reactions. The theory in question was originally formulated by Polyakov in connection with a study of the kinetics of the decomposition of potassium chlorate mixed with manganese dioxide, and of the ignition of the explosive hydrogen-oxygen mixture in the presence of platinum or palladium. According to this theory, homogeneous gas reactions originate under heterogeneous conditions, while heterogeneous reactions are transformed either into homogeneous reactions proceeding in stages or into chain-radical processes.

To confirm the correctness of these views, several series of investigations were carried out.

The first group of these investigations dealt with processes of incomplete and slow catalytic combustion, and incomplete explosive combustion. The method of igniting the mixture by means of an incandescent filament and capturing the intermediate products (peroxides, aldehydes, etc.) at a low temperature was used. In this work, the heterogeneous-homogeneous nature of the formation of the intermediate products was proven for the first time.

A long series of subsequent investigations dealt with the kinetics and mechanism of the slow and the explosive combustion of hydrogen, methane, carbon monoxide, and other substances. The effects exerted on the velocity of these reactions by the nature and state of the surface of the walls, by catalyst poisons, and by platinum rods of different lengths were studied at the institute. It was established that the dependence of the kinetics of these reactions on the nature and state of the walls of the vessel is due to the origination and interruption of chains at the surface of the walls. This result directly confirms the operation of a heterogeneous-homogeneous mechanism.

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A number of investigations carried out at the institute was concerned with the homogeneous stage of the explosive combustion of hydrogen and methane in the presence of nitrogen. The relationships which were found brought clarity into problems connected with the degeneration of the chain mechanism into a thermal mechanism, the nature of the process of chilling of unstable products, etc.

In a series of investigations the catalytic oxidation of ammonia on platinum was studied under dynamic conditions. It was shown that the maxima, which occur on the curves expressing the dependence of the yield of oxides of nitrogen on the time of contact with the catalyst, are produced by the heterogeneous-homogeneous defixation of ammonia under participation of the walls of the reactor.

In work dealing with the kinetics of polymerization and copolymerization, data were obtained which indicate that these reactions have a heterogeneous-homogeneous character, proceed under participation of the walls of the vessels, and are of the autocatalytic (explosive) type.

In investigations on the oxidation of propane-butane mixtures conducted at the institute, it was established that these mixtures do not react when the walls of the vessel are covered with sodium chloride. Then the conditions necessary for the initiation of a homogeneous reaction are absent. Later analogous results were obtained at the Institute of Chemical Physics, Academy of Sciences USSR, in work on the oxidation of propane and at the State Institute of the Nitrogen Industry in work on the oxidation of methane.

The fact that homogeneous stages occur in heterogeneous catalysis was proven in a series of investigations carried out at the institute, with the aid of the method of separate calorimetry devised by Koval'skiy at the Institute of Chemical Physics, Academy of Sciences USSR. As objects of investigation served the reactions of the incomplete oxidation of methane, ethylene, methanol, and butane-propane in the presence of platinum, silver, vanadium pentoxide, boron oxide, or other catalysts covering the walls of the reactors in a thin layer. The experiments confirmed directly the occurence of heterogeneous-homogeneous stages in all of these catalytic reactions. The specificity of the action of catalysts was expressed in their capacity to lower the temperature of the reaction and the energy of activation, and also in their selective effect on the formation of different intermediate products containing oxygen. V. V. Shalya, T. P. Kornienko, Ya. V. Zhigaylo, V. I. Urizko, and M. A. Piontkovskaya participated in the work on this subject.

By 1929, M. V. Polyakov and others started at the institute a series of investigations dealing with adsorption phenomena and the preparation of adsorbents having a predetermined pore structure. In this work the effect of the structure of the pores on the adsorption properties were studied. Furthermore, methods for the preparation of silica gels of different porosities were developed. On the basis of this work, research by I. Ye. Neymark and his group was started in 1944. Detailed investigation by Neymark, and others, of the structure of many samples of silica gels, which differed with regard to their preparation, led to a new explanation of the mechanism by which the structure by hydrophilous adsorbents comes into being. According to this explanation, the porosity of a dry gel is determined by the degree of compression of the hydrogel during its dehydration. The compression of the hydrogel is effected by capillary forces, the operation of which depends principally on the surface tension of the intermicellar liquid. During the process of drying, the rigidity of the gel skeleton counteracts the effect of the capillary forces. This rigidity, in turn, is determined by the hydrophilous quality of the particles entering into the composition of the gel. On the basis of these concepts it was possible to develop reproducible methods of preparing gels that have different types of porosity and obtain new structural types of silica gels as well as mixed adsorbents, e.g., alumosilica gels, etc. Some of the methods for the preparation of adsorbents, which had been developed at the institute, were introduced into industrial practice and are also being used in research work conducted at the leading USSR laboratories.

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In the work done by Neymark and others more precise methods for investigating the structure of porous adsorbents were developed; a system for the classification of adsorbents according to structural types was formulated and developed; the mechanism of the inactivation of adsorbents by heat was clarified; and a number of specific properties of mixed adsorbents were elucidated.

Work on the Chemistry of Isotopes

In 1934, soon after the discovery of deuterium, work on the chemistry of isotopes was begun at the institute. This work has been continued up to the present day. A. I. Brodskiy and his collaborators (O. K. Skarre, V. A. Aleksandrovich, M. K. Shelud'ko, Ye. I. Dontsova, Zh. M. Shershever, S. G. Demidenko, L. V. Korchagin, and others) were the first to obtain pure heavy water in the USSR (in 1934) and to prepare concentrated heavy oxygen (in 1937). These were used in various investigations. In connection with this work, a general theory of fractionation was developed and checked experimentally. The correctness of this theory was confirmed on many experimental examples. In a number of cases, application of this theory was found to replace to advantage the cumbersome methods of calculation proposed by foreign scientists. During 1934-1941, some physical constants of heavy water were determined and the exchange reactions of hydrogen isotopes investigated. Specifically, it was established that there is a rapid exchange in amino-groups and in the hydroxyl-groups of phenols. A statistical theory of the equilibrium distribution of isotopes was developed for compounds which have several exchangeable atoms in the molecule.

Considerable attention was paid to the isotopic composition of natural waters. Many published data which were based exclusively on density measurements were not of much value from the scientific standpoint, because the total change in the density of water is produced by two independent factors: the content of deuterium and the content of heavy oxygen. A precise method was developed at the institute for the separate determination of both heavy isotopes by means of simultaneous interferometric and density measurements, the latter with the aid of a float. By means of this method it was established that water obtained by the melting of snow has a lowered content of deuterium in comparison with the waters of rivers, lakes, springs, and the moisture of the air. On the other hand, the heavy oxygen content of snow water is normal. The isotopic composition of mountain rivers and mountain lakes, which are fed directly by melting snow, is the same as that of snow water. It was further established that river ice, just like artificial ice, has a noraml isotopic composition. These differences in composition, which are connected with the conditions under which moisture crystallizes in the atmosphere, have not yet been explained in a satisfactory manner. A study of arctic waters of which samples were collected by USSR arctic expeditions, showed that these waters can be divided into several sharply distinct groups, the isotope composition of which depends on orological conditions and the age of the ice. The isotope composition remains uniform along sea currents for thousands of miles.

In 1940, at the initiative of the institute, the first conference in the USSR on isotopes was held by the Academy of Sciences USSR, under the direction of V. I. Vernadskiy.

The use of isotopes as tracers in the investigation of the mechanism of chemical processes and in the study of the structure of molecules was begun in 1939, and resumed on a wider scale in 1945 with the participation of G. P. Miklukhin, I. P. Gragerov, B. A. Geller, A. S. Fomenko, I. A. Makolkin, L. L. Chervyatsova, A. F. Rekasheva, I. I. Kukhtenke, L. V. Sulima, and others, Some rearrangements and tautomeric transformations were investigated, and the following results obtained: the absence of tautomerism in toluene, phosphorous acid, the

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salts of phosphorous acid, and the alkyl esters of phosphorous acid was definitely proven, and its presence in hypophosphorous acid established. The intramolecular mechanism of the orthorearrangement of allyl esters (Claisen rearrangement) and the bimolecular mechanism of the rearrangement of oximes proceeding [by interaction of one molecule of the oxime with one molecule of water] under hydration and dehydration (Beckmann rearrangement) were established and clarified.

A new type of rearrangement of phenols was discovered which consists in the intramolecular exchange of hydrogen between the hydroxyl group and the hydrogens occupying the ortho and para positions in the nucleus. A systematic investigation of the reduction of ketones, diazonium salts, and phenyl hydrazine with alcoholates demonstrated that the reduction is effected by transfer of hydrogen atoms attached by C-H bonds, rather than the transfer of hydrogen atoms attached by O-H bonds in the hydroxyl groups of the alcohol or water. The exchange of identical radicals between alkyl halides, ethers, and dimethyl sulfate was investigated. With the aid of deuterium, the mechanisms of the photochemical and thermal decomposition of diphenylmercury and phenylmercury hydroxide were compared. This investigation was carried out in collaboration with Prof G. V. Razuvayev.

Significant results were obtained by using isotopes in research pertaining to the theory of chemical structure. It was established with the aid of deuterium that the H-atoms forming the hydrogen bonds in benzoquinhydrons are located at the hydroquinone nucleus. On heating, there is a tautomeric transformation in the course of which the H-atoms forming the bonds are transferred individually to the quinone nucleus after passing a potential barrier of 30 kilocalories per gram-mol.

The effect of the conjugation of bonds in salts of carboxylic acids was disclosed. This effect is expressed in the circumstance that the mobility of alpha-hydrogen atoms is decreased as the polarity of the O-X bond (where X stands for a metal or radical) increases. The application of this effect led to a new variation of the Perkin reaction carried out without acetic anhydride. If in the hydrogen exchange by acetates the heavy water is replaced by heavy acetic anhydride, the effect that has been described is reversed, as can be expected on the basis of theoretical considerations.

A new general theory of hydrogen exchange in solutions has been developed. This theory connects the rate of exchange with the structure of the electron shell of the atom to which the hydrogen being exchanged is bound. This theory was confirmed by studying the hydrogen exchange of ammonium salts, phosphites, hypophosphites, and also of Si-H groups of organosilicon compounds. The use of the heavy isotopes of hydrogen and oxygen made it possible to establish that there are significant differences between the behavior of [purely] organic compounds and that of the corresponding organosilicon compounds. These differences are due to the opposite polarities of the C-H and Si-H bonds.

During recent years particular attention was paid to the investigation of sulfur compounds with the aid of radioactive sulfur. It was established in work done under participation of G. A. Blokh that acceleration of the vulcanization of rubber by Captax (2-mercaptobenzothiazole) is brought about by the transfer of sulfur originating from exchange in the sulfhydryl group of the Captax accelerator. This exchange is apparently connected with a tautomeric transformation of the Captax molecules. Furthermore, the mechanisms of the reactions of the formation and decomposition of trithionates were clarified. This brought clarity to a question which could not be solved previously by a number of chemists.

It has been established by D. N. Strazhesko's work that electrochemical adsorption, i.e., adsorption that does not depend on the sign of the charge at the surface of the adsorbent, takes place on carbon not only in water but also in a number of nonaqueous solvents. This confirmed the applicability of A. N. Frumkin's electrochemical theory of ionic adsorption to nonaqueous solutions and considerably extened the field of this theory's application. With the aid of radioactive isotopes the fundamental laws of the electrochemical adsorption of ions from highly diluted aqueous and nonaqueous solutions were investigated. The results that had been obtained led to the development of a new method of preparative microchemistry, which made it possible to solve a number of important problems. Furthermore, the similarity between the orientation of polar organic molecules at the surface carbon and their orientation at other phase boundaries was demonstrated. These investigations led to the introduction into industrial practice of a substantially improved technique for the purification of therapeutic preparations by adsorption.

Work in the Field of Photochemistry

The photochemical research which was begun at the institute about 1929 at Pisarzhevskiy's initiative represented further developement of his ideas on the electronic mechanism of elementary process of oxidation and reduction. These ideas received a direct confirmation in work done by B. Ya. Dain and his collaborators (M. S. Ashkinazi, T. S. Glikman, A. A. Kachan, B. F. Kutsaya, and others) on the primary processes which are induced by light quanta in solutions.

The most sifnificant results were obtained in the investigation of photo-processes taking place in solutions of electrolytes. In this work the specific type of elementary photochemical process was discovered and investigated in which electrons are transferred by light quanta from particles of one kind to particles of another kind in the immediate vicinity. This type of light-induced transfer was investigated in detail on the ions $C_2O_4{}^{2=}$, Fe^{2+}, and Cr^{2+}.

Analysis of the kinetic data pertaining to these processes, as well as of the regularities in the spectra of the ions involved, indicates that the water molecules of the hydrate envelope serve as receptors of the electrons in all cases. It was shown that the development of hydrogen, which is observed in reactions of this type, is a result of the decomposition of the water of the solvent. It was also established that there is a simple relationship between the position at the end of the long-wave region in the spectra of the electron transmission of ions and the redox potential of the systems under investigation. The nature of the so-called active oxalic acid was clarified for the first time. In the light of the data obtained, a general explanation of the volume photogalvanic effect could be given. This effect is observed specifically in oxalate solutions.

The second type of the photochemical transfer of electrons was studied after World War II on ions of the oxidized type, e.g., Fe^{3+}, Cu^{2+}, and Ce^{4+}. It was established that the action of light quanta on these ions brings about their photochemical reduction by transfer of electrons to them from the water molecules, which decompose under the formation of oxygen. On the example of Ce^{4+} ions, the effect of the walls of the vessel on the light-induced transfer of electrons was demonstrated.

The third type of elementary processes of this kind, i.e., processes involving transfer of elctrons within complexes, was investigated in research on the photochemistry of complex oxalates. The investigation of the spectra and of the photochemical behavior of 12 complex compounds of this class led to the conclusion that only those in which the transfer of electrons is possible are subjected to photochemical decomposition. This conclusion has general validity in the photochemistry of complex compounds.

The photochemical reactions which involve electron transfers as well as the spectra that pertain to these reactions were also investigated on the alcohol solutions of a number of salts. On the basis of the relationships which had been established, a general concept was formed in regard to the dependence of the position of ion adsorption bands on the donor and acceptor characteristics of the solvent.

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On the basis of the data obtained in regard to the photoinduced reactions of electron transfer, it was shown that almost all known reactions which take place in electrolyte solutions involve transfer of electrons in the primary stage of the reaction. The same data were used in establishing general relationships which pertain to the mechanism of redox reactions taking place in the dark.

With the purpose of establishing the mechanism of the photochemical redox transformations that are characteristic for organic systems, in which transfer of hydrogen is the immediate result of the action of light, the photochemical reduction of some oxazine and thiazine dyestuffs was investigated and the photooxidation of their leucoforms was studied. It was established that the processes involved are subject to general laws which are in agreement with A. N. Terenin's concept that the photochemical transfer of hydrogen proceeds in two stages, of which the first stage is the photoinduced transfer of an electron. It was shown on several examples that introduction of a metal into the molecules of colored substances (azodyestuffs, pheophytin, and pheophorbide) causes sharp changes of the activity of these substances in photochemical redox reactions.

When iron salts were reacted with pheophytin or pheophorbide, oxidized and reduced iron-containing analogs of chlorophyll were obtained. These analogs were found to undergo mutual transformation as a result of the action of quanta of visible light. This result is of interest from the standpoint of the theory of photosynthesis, because in the organism of plants all prerequisites exist for the formation of complex compounds of this type, while the mutual photochemical transformations of these complexes indicate that the transformations in question may participate in the sensitization leading to reactions, which occur in the first stage of the photosynthesis.

Work on the Structure of Liquids

From 1927 to 1930, V. I. Danilov, together with A. Z. Golik and others, began basic research on the structure of liquids, using X-ray methods. Since 1946, Golik has continued this work at the institute.

At present, neither a quantitative theory of the liquid state nor a molecular theory of the viscosity of liquids exists. Because specific difficulties interfere with the formulation of these theories, a number of physicists acquired the impression that fundamental obstacles of a theoretical nature make the formulation of a quantitative theory of the liquid state impossible. A new approach to the problem became necessary. This new approach is outlined in Golik's work, who has advanced the idea of studying the molecular structure of liquids and the mutual interdependence of the physical properties of matter in the liquid state.

From this standpoint extensive experimental investigations have been carried out on the viscosity, density, critical temperatures, latent heats of evaporation, X-ray structure, and the solubility of pure liquids and of their binary and ternary solutions. The dependence on the molecular structure of the viscosity, density, and critical temperatures of a large number of organic liquids and their solutions of the molecular mixture type was subjected to study. Solutions of electrolytes were also investigated from this standpoint. New relationships were established for the dependence of the properties enumerated on the temperature and the concentration. It has been found that these properties depend on the molecular structure.

Analogous investigations were carried out on solutions the components of which interact chemically with each other. It was established that different, much more complicated relationships apply to solutions of this type.

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New data were obtained on the structure of liquids and a method was developed for the calculation of some physical properties of liquids on the basis of their function of radial distribution.

Collation and evaluation of the results showed that knowledge of the coordination number and of the radius of the first coordination sphere only is not adequate for the characterization of the structure of a liquid substance: one must introduce an additional parameter which characterizes the interaction between molecules and is closely connected with the critical parameters [constants] of the substance. Thus, the critical temperature characterizes macroscopically the third parameter, which together with the coordination number and the radius of the first coordination sphere, determines the structure of a liquid. The concept of the molecular structure of matter in the liquid state has been introduced, a concept which takes into consideration not only the geometric, but also the dynamic characteristics of the microstructure of a liquid, i.e., the type of molecular interaction in it. A simple method for characterizing liquids on the basis of their molecular structure has thus been introduced and is being applied.

Furthermore, it has been shown that within the limits of classes of liquids that have a similar molecular structure simple relationships exist which characterize the dependence of physical properties on the temperature and the interdependence of these properties on each other. On the basis of these considerations, workers at the institute predicted and discovered the existence of the so-called isoviscous liquids which have different compositions, but an identical viscosity throughout the whole temperature range of the existence of the liquid phase.

When the components of a solution differ with respect to their molecular structure, and particularly when they interact with each other, simple relationships for the dependence of physical properties on the temperature and the concentration do not apply, nor are isoviscous liquids formed.

From 1940 to 1948, M. F. Vuks, who studied the Rayleigh dispersion and Raman dispersion spectra within the low frequencies range in crystals and liquids, obtained proof that the lines of low frequency in spectra of organic crystals are produced by rotary oscillations of the molecules in the lattice. On the basis of the correspondence between low frequency spectra of crystals and liquids, the conclusion was made that the molecular dynamics of liquids are similar to the dynamics of crystals. Furthermore, a new method was developed for the investigation of the composition of the Rayleigh emission spectrum and of the low frequency spectrum, namely the method of resonance filtration. This method aided in obtaining complete data on the distribution of intensities in the region of the Rayleigh lines of some liquids.

Work in Other Fields

In work done at the institute considerable attention was paid to the application of physicochemical methods of analysis in production control.

From 1930 to 1941, A. M. Zan'ko and others, who worked on the theory of potentiometry, proposed the following methods for practical application at plant laboratories: a potentiometric method for the complete analysis of manganese ores; a polarographic titration method for the determination of magnesium in dolomites; and rapid methods for the polarographic determination of metals. Zan'ko and his group carried out a number of investigations on the application of organic reagents in analysis, and on conductometric and interferometric analysis. With the participation of V. F. Stefanovskiy, the kinetics of rapid redox reacions were studied.

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From 1937 to 1949, work on physicochemical methods of analysis was also conducted by M. S. Ashkinazi. During a number of years she and her collaborators worked on the development of method for the quantitative analysis of ferrous metals, nonferrous metals, and alloys by emission spectroscopy. The introduction of these methods into practical use was expedited during World War II. As a result of this work, determination of metals with the aid of a single standard or without a standard became possible, and procedures of this type were adopted in practical industrial plant control.

Under the direction of A. L. Davydov and with the participation of Z. M. Vaysberg, new, precise, and sensitive photocolorimetric methods for the determination of phosphorus, vanadium, silicon, tungsten, molybdenum, and arsenic were developed during 1936-1950. These methods were introduced into practical use at plant laboratories on a wide scale. Z. M. Vaysberg developed methods for the determination of columbium and titanium in steels, and of cerium in minerals. For this purpose the color reactions connected with the formation of various derivatives of tungsten blue and molybdenum blue were used. To clarify the chemical nature and structure of these blue compounds, B. Ya Dain and Z. M. Vaysberg subjected them to spectroscopic examination and found that they belong to a special class of heteropolyacids, which have reduced coordination groups.

From 1934 to 1941, F. I. Berezovskaya and Ye. K. Varfolomeyeva, who conducted investigations on the kinetics of reactions in solutions, studied the effect of various additions on the thermal decomposition of peroxides.

During the postwar years (1944-1949), P. P. Budnikov carried out investigations on the physical chemistry of silicates. As a result of work done by Budnikov, a method was developed for the production of gypsum alpha-hemihydrate, a substance which has a very high index of mechanical strength; a new type of highly refractory chromodolomite was obtained; and a method was developed for the preparation of tricalcium silicate (alite), a cement which has a very high mechanical strength.

From 1927 to 1930, G. V. Korshun and K. V. Roll conducted research on the adsorption spectra of a number of pyrrol derivatives and found that these spectra depend on the constitution of the compounds in question.

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