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HISTORY OF CHEMISTRY AND CHEMICAL TECHNOLOGY =

Academician Lev Vladimirovich Pisarzhevskii (To 130th Anniversary of His Birthday)

L.V. Pisarzhevskii, a scientist, pedagogue, research organizer, and public figure, is one of the most prominent Russian physical chemists of the first half of the XX century. His studies covered a wide variety of problems: chemistry and structure of metal peroxides, nonaqueous solutions, electronic theory of redox processes, and theory of catalysis.

Lev Vladimirovich Pisarzhevskii was born on February 14, 1874, in Kishinev, Bessarabia Province, into the family of a notary. In 1882, after his father's death, the family moved to Odessa, where Pisarzhevskii finished a classical gymnasium and entered the naturalmedical faculty of Novorossia University (Odessa). Soon afterwards, however, he went to the chemical department of the physicomathematical faculty and all his subsequent scientific and pedagogical activities were associated with chemistry. Among his teachers at the University were such well-known scientists of that time: A.A. Verigo (1837-1905), P.G. Melikishvili (1850-1927), S.M. Tanatar (1849-1917), and P.I. Petrenko-Kritchenko (1866-1944). Already beginning with his second term at the University, Pisarzhevskii commenced research work under the supervision of professor Melikishvili, analyzed the composition of a meteorite, and later studied peroxy compounds. In 1896, Pisarzhevskii graduated from Novorossia University with first-degree diploma and, on recommendation of professors Verigo and Melikishvili, was left at the university to be trained for professorship.

In 1898, the young scientist passed master's examinations and gained a right to deliver lectures as privatdocent. The courses of lectures, planned to be delivered by him, covered the topical problems of physical chemistry, which originated at that time. In 1899, Melikishvili and Pisarzhevskii were awarded the Lomonosov Prize for the monograph Issledovaniya nad perekisyami (Studies of Peroxides). In January 1901, Pisarzhevskii was sent to a business trip to Leipzig, to the laboratory headed by W. Ostwald (1853-1932, 1909 Nobel Prize in chemistry), which was the renowned center of novel ideas and research in physical chemistry at that time. Quite a number of young Russian scientists worked in Leipzig in different years [1, 2]. In the early XX century, the main areas of research conducted by Ostwald and his closest associates were kinetics and catalysis.



At Ostwald's laboratory Pisarzhevskii finished work on his master's dissertation "Peroxides and Peracids," which he successfully defended at Novorossia University on November 20, 1902 [3].

Various peroxide compounds, objects of study of inorganic chemistry, were examined using physicochemical methods, electrical conductivity measurements, as well as thermochemical and kinetic techniques. As a theoretical substantiation served Arrhenius's theory of solutions and the laws of thermochemistry. Melikishvili and Pisarzhevskii studied a wide variety of peroxide compounds, including quite a number of substances synthesized by them for the first time. The structural similarity of hydrogen peroxide, metal peroxides, and peracids was demonstrated. Metal peroxides were regarded as salts of hydrogen peroxide, in which it plays the part of a mono- or dibasic acid. Peracids were regarded as mixed anhydroacids of common acids and hydrogen peroxide. D.I. Mendeleev was much interested in the studies of peroxide compounds. In 1897-1899, Melikishvili and Pisarzhevskii published in co-authorship 16 studies concerned with peroxide compounds; 11 more investigations in this area were published by Pisarzhevskii alone in 1900–1903. The scientist reverted to the subject of peroxide compounds more than once in the subsequent years. A detailed analysis of investigations carried out at Novorossia University by the founders of chemistry of peroxide compounds was made in Turchenko's monograph [4] and in [5, 6].

On January 1, 1903, were commenced diverse Pisarzhevskii's pedagogical activities at Novorossia University. He delivered courses of lectures in inorganic and analytical chemistry to students of various specialties and supervised practical studies in physical chemistry, organized by himself. It so turned out that Pisarzhevskii's work at Novorossia University was not long. In 1903, G. Tammann (1861-1938) moved to Germany, to Göttingen University, and freed the chair of chemistry at Yur'ev (Tartu) University. In the second half of the year of 1904, Pisarzhevskii was invited to this chair as extraordinary professor. Already in the 1904/1905 academic year, he delivered all the lectures in chemical disciplines at the physicomathematical faculty. However, the unfavorable conditions for research work, the lack of necessary equipment, the political circumstances of that time, and the Baltic climate, taken together, resulted in that Pisarzhevskii returned to the Ukraine at the beginning of 1908 to fill a vacant position of a professor of inorganic and analytical chemistry at Kiev Polytechnic Institute.

Nevertheless, Pisarzhevskii in fact started at Tartu the second series of his experimental studies of chemical interaction of solutes with a solvent [5, 7]. In 1904–1908, he published five papers in this field. The area of research, chosen by the scientist, was characteristic and rather important for the understanding of the nature of solutions at the turn of the XX century. Undoubtedly, this choice was affected by the two years' stay of Pisarzhevskii at Ostwald's laboratory. The theoretical concepts of solutions, developed by J. Vant-Hoff (1852-1911, 1901 Nobel Prize in chemistry) and S. Arrhenius (1859–1927, 1903 Nobel Prize in chemistry) provoked objections of a number of leading Russian scientists. Being a supporter of Arrhenius's theory, Pisarzhevskii was aware of the necessity for supplementing this theory with account of Mendeleev's views on the chemical nature of solutions. In his publications, Pisarzhevskii aimed at avoiding the extreme opinions of advocates of the physical and chemical theories of solutions. A detailed analysis of the nature of the difference in opinions was made in Solov'ev's monograph [8] and in some other publications [3-5, 9].

To elucidate the role of chemical factors in solution formation, Pisarzhevskii did not restrict his consideration to a study of solutions in various solvents, as it was done by other scientists concerned with this problem. Contrariwise, he undertook wide-scale investigations of the influence exerted by the solvent on the chemical equilibrium. He studied nine ionic reactions in 47 simple and mixed solvents and calculated more than 100 equilibrium constants [5, 9]. The equilibria were studied both analytically and by measuring the electromotive forces of appropriate circuits. When necessary, the electrical conductivity and viscosity were also measured. It was established that the solvent strongly affects the state of equilibrium. Pisarzhevskii himself formulated the basic conclusion made on the basis of this series of investigations as follows: "... it is necessary to recognize the chemical interaction between the solvent and solutes and to regard the dissolution process as purely chemical phenomenon" [10, 11]. This chemical phenomenon consists in solvation.

Having started lecturing at Kiev Polytechnic Institute in April 1908, Pisarzhevskii paid considerable attention to improvement of the teaching process. He introduced a theoretical course "Introduction into Analytical Chemistry," delivered lectures in terms of the ionic theory, and redesigned the system of practical works in analytical chemistry. In 1908–1911, Pisarzhevskii finished work on his doctoral dissertation "Free Energy of a Chemical Reaction and the Solvent" [10], which he defended successfully at St. Petersburg University in 1913.

Already when being a professor in Tartu, Pisarzhevskii belonged to a revolutionary all-Russian Akademicheskii Soyuz (Academic Society). In 1911, in connection with political unrest in quite a number of higher-school institutions, Pisarzhevskii resigned, together with a group of professors of the Polytechnic Institute, and moved to Moscow, to become there one of founders and editors of a popular-science journal *Priroda* (Nature). At that same time, Pisarzhevskii delivered lectures at Bestuzhev school and Institute of Psychoneurology in St. Petersburg.

In 1913, Pisarzhevskii was elected a professor of general and physical chemistry at the Mining Institute in Yekaterinoslav (now Dneropetrovsk), and all the subsequent pedagogical and scientific activities of the scientist were associated with this institute. Already during the first years of his work there, the third and, probably, the main area of Pisarzhevskii's research was formed: the electron in chemistry and the nature of redox processes. He published a series of articles "The Electron in Chemistry of Solutions and in Electrochemistry" (1921-1924) and a monograph under the same title (together with M.A. Rozenberg, 1923). As far back as 1914, Pisarzhevskii demonstrated that all chemical processes can be regarded as a result of electron transfer from some atoms or molecules to others, with the interaction of the free electric charges that are generated in the process [9]. The oxidation and reduction processes were interpreted as transfer of electrons from an oxidant to a reducing agent. All these approaches were introduced by Pisarzhevskii and his closest associates into the teaching process and described in understandable form in the textbooks Vvedenie v khimiyu na osnove stroeniya atoma i elektronnogo stroeniya molekul, chast' 1 (Introduction into Chemistry on the Basis of Atomic Structure and Electronic Structure of Molecules, Part 1) (Dnepropetrovsk, 1928) and Neorganicheskaya khimiya (Inorganic Chemistry) (together with Rozenberg; Dnepropetrovsk, 1930; Kharkov, 1933 and 1934).

The concept of redox processes was extended to reactions in solutions, heterogeneous catalysis, and electrochemistry. For his investigations in the field of electronic chemistry, Pisarzhevskii was awarded a Lenin Prize in 1930.

In addition to the Mining Institute, Pisarzhevskii taught at other higher-school institutions of Yekaterinoslav: Institute of People's Education and Medical Institute. In 1923–1926, he held the position of rector of the Mining Institute. In 1922, on Pisarzhevskii's initiative, a research chair of electronic chemistry was created at the Mining Institute. Already in 1927, this chair was reorganized into Ukrainian Research Institute of Physical Chemistry, and in 1934, into the Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR (Soviet Socialist Republic). In 1936, the institute was named for L.V. Pisarzhevskii.

In 1925, Pisarzhevskii was awarded a title of Honored professor of the Ukrainian SSR. In the same year, he was elected a full member of the Academy of Sciences of the Ukrainian SSR. He was elected a corresponding member of the Academy of Sciences of the USSR in 1928, and a full member of the Academy in 1930. The contribution made by the scientist to the development of higher technical education in the Ukraine is remarkable. On Pisarzhevskii's initiative, a faculty of chemical engineering was opened at the Mining Institute and the metallurgical faculty was developed further. In 1930, during the period of reorganization of the higher-school institutions in the country, the Institute of Chemical Engineering and Metallurgical Institute were created on the basis of these faculties.

In 1929, Pisarzhevskii was invited to Georgia to create at Tbilisi a chemical research center. This aspect of the scientist's activities has been considered in detail by A.Sh. Avaliani and co-authors [12]. In 1928, the State Polytechnic Institute of Georgia was organized in Tbilisi. This institute, in particular, included a mining-chemical faculty with two departments, mining and chemical. The chemical department was intended to train chemists-technologists and metallurgists. Pisarzhevskii and his closest associate Rozenberg were entrusted with organization of teaching of all the chemical disciplines at the due level. Simultaneously, Pisarzhevskii was engaged in organization of the Research Institute of Chemistry, officially opened on October 1, 1929. Pisarzhevskii was appointed the director of the Institute, and Rozenberg, the head of the department of electronic chemistry. As suggested by the director, the Institute was named after Melikishvili. The stay of Pisarzhevskii in Tbilisi was not long; it coincided with the reorganization of the higher school and scientific institutions in the country, but exerted strong influence on the subsequent development of chemical research in Georgia [12]. In the summer of 1931, Pisarzhevskii returned to Dnepropetrovsk, with, however, his intimate contacts with Georgian colleagues maintained. In 1934, Pisarzhevskii again headed the Institute, which was then already a part of the Georgian branch of the Academy of Sciences of the USSR, for a short time.

Among Pisarzhevskii's pupils and closest associates in the Ukraine were the following, later wellknown scientists: A.I. Brodskii (1895-1969, academician of the Academy of Sciences of the Ukrainian SSR since 1939, corresponding member of the Academy of Sciences of the USSR since 1943), a prominent specialist in chemistry of isotopes and author of the textbook Fizicheskaya khimiya (Physical Chemistry), which ran into numerous editions; V.A. Roiter (1903–1974, academician of the Academy of Sciences of the Ukrainian SSR since 1961), author of the monograph Vvedenie v teoriyu kinetiki i kataliza (Introduction into Theory of Kinetics and Catalysis) (1971); and S.Z. Roginskii (1900–1970, corresponding member of the Academy of Sciences of the USSR since 1939), the founder of a prominent scientific school specialized in the theory of catalysis.

Pisarzhevskii was actively involved in public and political activities in the country and was a member of executive Soviet bodies: he became an alternate member of the Central Executive Committee of the USSR in 1928, was elected a member of the Central Executive Committee of Georgia in 1930 and 1935, and became a member of Central Executive Committee of the Ukraine in 1935.

Academician Lev Vladimirovich Pisarzhevskii died of a severe illness on March 23, 1938, in Dnepropetrovsk. A vast literature is devoted to his life and scientific activities. Of particular value are papers written by the closest associates of the scientist: Rozenberg, Brodskii, B.Ya. Dain, Roiter, and S.Z. Roginskii [3, 5, 13–15]. Considerable attention was given to Pisarzhevskii's works in the well-known monographs devoted to the development of chemical science in Russia [8, 9, 16, 17] and in the Ukraine [4, 18, 19]. A popular-science sketch of Pisarzhevskii's life and scientific activities has been written by Yu.S. Lyalikov [20]; other popular-science publications are also available [6, 21, 22].

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A.G. Morachevskii