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On 150th Anniversary of the Birthday of Academician V.A. Kistyakovskii[1]

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September 30 (October 12), 2015, was the 150th anniversary of the birth of an outstanding scientist in the field of physical chemistry, electrochemistry, and corrosion of metals: Academician Vladimir Aleksandrovich Kistyakovskii. He was born in Kiev in a very well–educated family, of which several members later became quite famous. The head of the family, Alexander Fedorovich Kistyakovskii (1833–1885), was one of the most prominent criminalists in Russia, Professor of Criminal Law in Kiev University.

In 1883, V.A. Kistyakovskii successfully graduated from the 2nd Kiev Secondary School and entered the Natural Department of Physical–Mathematical Faculty of Kiev University. However, already in autumn of 1884, he became interested in chemistry and transferred to a similar Department of St. Petersburg University, where D.I. Mendeleev, A.M. Butlerov, N.A. Menshutkin and other leading scientists were teaching at the time.

As advanced undergraduate, V.A. Kistyakovskii worked under the guidance of Professor M.D. L'vov, a student and a closest assistant of A.M. Butlerov. Already in 1889, the first scientific work of V.A. Kistyakovskii, "Effect of Aqueous Solutions of Arsenic Acid on Liquid Isobutylene and Amylene" (Lecture of M. L'vov, Protocol of the Meeting of the Chemistry Department of Russian Physico-Chemical Society, May 4, 1889), was reported at the Meeting of the Russian Physico-Chemical Society. This was the only work of V.A. Kistyakovskii in the field of organic chemistry. Further, his scientific interests shifted wholly to physical chemistry under the influence of the works of J. Van't Hoff, M. Planck, S. Arrhenius. In 1884–1887, the most important studies of these scientists in the field of the solution theory and related issues were published. The first volume of the new international physico-chemical journal, "Zeitschrift für Physikalische Chemie" published in February of 1887 contained the paper of a young Swedish scientist, Svante Arrhenius "On Dissociation of Substances Dissolved in Water." The initiator of publishing the journal was W. Ostwald (1853–1932).

The laboratory of W. Ostwald in Leipzig University became the center of new trends in physical chemistry: Arrhenius theory of electrolytic dissociation, Van't Hoff osmotic theory, the theory of catalysis developed by Ostwald himself. W. Ostwald was one of the first, already in 1884, to esteem very favorably the work of S. Arrhenius on electrolytic dissociation and under-

[1] The paper is dedicated to the memory of academician V.A. Kistyakovskii (1865–1952).

stand that it contained new approaches that could produce great effect on the development of the solution theory and electrochemistry.

At the same time, the work of S. Arrhenius was rejected by the leading Russian scientists of the time: D.I. Mendeleev, D.P. Konovalov, N.N. Beketov and others. Mendeleev never, till the end of his life, accepted the concepts developed by S. Arrhenius. Young V.A. Kistyakovskii thought differently. He showed great interest to the new approaches to the nature of solutions of electrolytes and his diploma work, by agreement with the Faculty Dean, N.A. Menshutkin, was a review entitled "Hypothesis of Planck–Arrhenius." This was one of the first works in Russia relating the opinions of a group of Western scientists on the nature of solutions of electrolytes and dissociation processes. In the final section of the work, V.A. Kistyakovskii discussed the possibility of bringing together different approaches to the nature solutions on the basis of the idea of ionic hydration.

A number of scientists in Russia supported the ideas of Arrhenius. These included in particular Professor of Riga Polytechnical Institute P.I. Valden, well known St. Petersburg physicists I.I. Borgman, O.D. Khvolson, Professor of Moscow University I.A. Kablukov.

On January 30, 1889, V.A. Kistyakovskii successfully graduated from the Natural Department of Physical–Mathematical Faculty of St. Petersburg University, received the Candidate's degree and, while he had no prospects regarding work, he went on his own initiative to Leipzig, Germany, to the laboratory of W. Ostwald. At first, he worked as a student; then he studied conductivity of aqueous solutions of double salts under the guidance of S. Arrhenius. It was V.A. Kistyakovskii who introduced the concept of complex ions in aqueous solutions into the Russian literature. In 1890, this work was published in Russia and in Germany. V.A. Kistyakovskii became acquainted in Ostwald's laboratory, apart from W. Ostwald and S. Arrhenius, with other leading physico-chemists of the time: J. Van't Hoff, W. Nernst. After working in Leipzig, V.A. Kistyakovskii listened to a course of lectures in physics in Paris University.

In November of 1890, V.A. Kistyakovskii returned to Russia. He performed experiments in the chemical laboratory of St. Petersburg university, passed a master exam and published the two–part large study of "Chemical Conversions in a Uniform Medium at Constant Temperature," in which he generalized the data of his experiments in the field of the kinetics of etherification reactions in aqueous–alcohol media. The kinetic studies of V.A. Kistyakovskii continue the works of W. Ostwald, J. Van't Hoff, D.P. Konovalov on mathematical description of the rate of various complex reactions.

After reading two test lectures in 1896, with account for the master exam, V.A. Kistyakovskii was allowed to teach in the university as a privatdozent; he was the first person in Russia to deliver lectures in some disciplines of physical chemistry: electrochemistry, photochemistry.

In 1898, V.A. Kistyakovskii published a large review work dedicated to the decade of the Theory of Electrolytic Dissociation. In this work, in particular, he pointed out great achievements of W. Ostwald who applied the mass action law to dissociation processes and established the law of variation of the relative number of electrolytically dissociated molecules and thus the values of conductivity under dilution.

The scientific community took a great interest in the report of V.A. Kistyakovskii on the topic of "Analysis of counterarguments to theory of electrolytic dissociation" delivered in XI Congress of Russian natural scientists and doctors in St. Petersburg on December 20–30, 1901.

In August of 1902, V.A. Kistyakovskii grounded the first Russian laboratory of physical chemistry and theoretical electrochemistry in the new St. Petersburg Polytechnical Institute that was to educate engineer electrochemists. After defending his Master's thesis in Moscow University, V.A. Kistyakovskii was appointed extraordinary professor. He delivered lectures in physical chemistry and theoretical electrochemistry, performed experimental studies having the then first-rate equipment, developed laboratory courses for students, guided diploma works. The period from 1903 to 1917 was the most productive time in the life of this scientist. The electrochemical practicum in Polytechnical Institute remained the best one in Russia for many years. In fact, all the main achievements of V.A. Kistyakovskii belong to this period. The central place in the whole scope of research trends followed by V.A. Kistyakovskii was studying the electrochemical behavior of metals in aqueous media.

Already in 1901, while determining the electrode potential of magnesium in a potassium cyanide solutions, V.A. Kistyakovskii observed for the first time the phenomenon of passivity for this metal. He studied the electrochemical behavior of magnesium in more detail in 1907. At first, the passive state of magnesium was ascribed only to formation of an invisible oxide film. Later, V.A. Kistyakovskii interpreted this process as formation of magnesium oxyhydrate. This led to consideration of thin films on the basis of colloid–electrochemical perspectives. Starting from 1909, the scientist developed his own original film theory of metal passivity and corrosion with respect to magnesium, iron, chromium, and particularly aluminum. The first generalization of the obtained experimental data was provided in the Doctoral (Chemistry) Thesis of V.A. Kistyakovskii that was published in full as a separate book "Electrochemical Reactions and Electrode Potentials of Some Metals." The thesis was defended in May of 1910 in Moscow University. Electrochemical studies, the explanation suggested by the scientist

regarding the causes of transition of metals into the passive state were highly praised by experts. Having obtained the degree of doctor of sciences in chemistry, V.A. Kistyakovskii was elected a full professor in physical chemistry and theoretical electrochemistry in Polytechnical Institute. Let us consider in mode detail the model of metal passive state and corrosion suggested by V.A. Kistyakovskii. Its basic provisions are that the studied metals are coated by an oxide film both in the active and passive states. The difference is only that in the passive state this film has an amorphous glassy structure, while in the active state it is partially destroyed due to corrosion processes. V.A. Kistyakovskii specially emphasizes that there is also an amorphous passivating film on metallically shiny surfaces of nickel, iron, chromium. The potentials of passive electrodes are considered as the oxygen potentials. V.A. Kistyakovskii offers the following description of the film forming on the metal: impenetrable for new portions of oxygen due to a relatively larger volume as compared to the specific volume of the metal, nonequilibrium by its structure (amorphous), conducting and invisible (glassy) due to its insignificant thickness.

One must point out that the final concepts of the passive film formation and its relationship to the corrosion processes were formulated by V.A. Kistyakovskii later, up to 1925. Transition from the passive state into the active state, in the opinion of the scientist, is accompanied either by partial decomposition of the amorphous film or film crystallization resulting in formation of pores. In the active state, the film does not completely disappear, only some of its regions are damaged. An oxidant helps restoring the film integrity, thus assisting the transition into the passive state. As opposed to M. Faraday and other researchers of metal passivity, V.A. Kistyakovskii believed that the presence of oxides on the metal surface alone is insufficient for metal transition into the passive state; the oxide film structure is important.

The problems of passivity are closely adjacent to the studies of V.A. Kistyakovskii on the effect of movement on the behavior of the metal immersed into the solution of electrolyte. These works are one of the first systematic studies of this kind. V.A. Kistyakovskii evaluated the occurring processes on the basis of variation of the electrode potential value. The phenomena which the scientist denoted as motochemical or motoelectric were based on the effect of the movement of the liquid on transition of the metal from the active state into the passive one. V.A. Kistyakovskii himself described these phenomena as follows: "We consider periodical phenomena as a fight between the amorphous state of the oxide film coating iron (passive state) and crystallinity corresponding to the active state ... periodical phenomena can be observed only under exceptionally favorable conditions."

In the same years (1912–1916), V.A. Kistyakovskii wrote and published in several separate parts a text book in electrochemistry, undoubtedly the most comprehensive course in electrochemistry in Russian for that time. Of the scientists whose names are related to development of electrochemistry in the first half of the XIXth century, V.A. Kistyakovskii specially pointed out J.J. Berzelius and M. Faraday.

In 1918, the classes in Polytechnical Institute were in fact stopped and V.A. Kistyakovskii decided to go to Kiev, where his mother and other relatives lived. In February of 1919, in Kiev, V.A. Kistyakovskii was elected the Fellow of The Ukrainian Academy of Sciences created under the direction of Academician V.I. Vernadskii. In 1920–1921, the scientist lived in North Caucasus, in Pyatigorsk, on medical indications. V.A. Kistyakovskii returned to pedagogical and scientific work in Petrograd Polytechnical Institute in the autumn of 1922.

In 1925, V.A. Kistyakovskii becomes the Corresponding Member of Academy of Sciences during scheduled elections in Academy of Sciences of the USSR. His recommendation for this rank signed by a group of academicians headed by N.S. Kurnakov describes the works of V.A. Kistyakovskii in the field of the nature of the liquid state, metal passivity, metal protection from corrosion. In January 1929, on the recommendation of the Commission consisting of Academicians N.S. Kurnakov and V.N. Ipat'ev, V.A. Kistyakovskii was chosen Fellow of Academy of Sciences of the USSR.

The main provisions of the film theory of V.A. Kistyakovskii were confirmed by studies of passivating films using different methods available in the first half of the XXth century. The results of studying films are considered in the work of P.D. Dankov (1946), one of the students of V.A. Kistyakovskii. The actual existence of passivating films as a phase-limiting substance layer differing from metal was confirmed by structural studies. The films had a colloid dispersion degree: their thickness was 2 to 20 nm; the films were transparent and became invisible when applied onto the metal surface. In the case of true passivation, the films were solid. Structural studies also confirmed an important provision of the theory of V.A. Kistyakovskii: the film is formed directly from solid metal and oxygen-containing particles and not by the secondary process of deposition of insoluble solution components. The film thickness exceeds the monomolecular oxide layer, which prevents considering it as adsorbed. The most interesting facts were obtained in studies of films using the electron diffraction technique.

The approach of V.A. Kistyakovskii to the problem of iron corrosion based on the film theory of metal passivity was first reported on the 2nd Congress of Scientists in Metallurgy dedicated to D.K. Chernov in Leningrad on May 25–June 3, 1924. The scientist

delivered a comprehensive lecture accompanied by demonstration of many experiments to the theme of "On Rusting of Iron."

In the final part of the lecture, V.A. Kistyakovskii emphasizes that "...the fundamental issue in protecting iron from rusting is developing conditions for preservation of a solid film passivating iron on its surface. Polished iron is already coated by a thin glassy oxide film." The best originators of a passivating film are solutions of the given concentration containing mixtures of alkali and oxidants.

In 1930, on the initiative of V.A. Kistyakovskii supported by Presidium of Academy of Sciences of the USSR, the Colloid–Electrochemical Laboratory (CECL) is formed in Leningrad. Its object at first was to study colloid–electrochemical phenomena, particularly to study dispersed systems, thin films, problems of corrosion, metal electrocrystallization. The closest colleagues of V.A. Kistyakovskii in CECL were A.N. Strel'nikov (Head of Department of Dispersion Chemistry), I.V. Krotov (Head of Department of Corrosion of Metals), K.M. Gorbunova (Head of Electrochemical Department). The students of V.A. Kistyakovskii in CECL were well known later electrochemists Ts.A. Adzhemyan, A.T. Vagramyan, physico–chemist P.D. Dankov.

In 1933, V.A. Kistyakovskii considered the problems of corrosion from the viewpoint of colloid electrochemistry in a review paper in the journal of "Uspekhi Khimii."

Together with a whole number of other academic institutions, CECL was transferred in 1934 to Moscow, expanded and soon transformed into Colloid–Electrochemical Institute (CEIN). The Director of CEIN from 1939 to 1949 was Academician A.N. Frumkin. In 1946, CEIN was transformed on his initiative into Institute of Physical Chemistry of Academy of Sciences of the USSR, the largest scientific center of the country.

Studies of V.A. Kistyakovskii in the field of physical chemistry and electrochemistry are diverse; the scope of his scientific interests is wide, but his role in the history of the national science is primarily that of the first Russian electrochemist who did a lot for advancement of the progressive electrochemical concepts of his time, the creator of the first specialized educational and scientific laboratory in the field of physical chemistry and electrochemistry in Russia. It was a well informed scientist that enjoyed a great reputation not only in our country, but also abroad.

Vladimir Aleksandrovich Kistyakovskii died on October 19, 1952, when he was 87, after a prolonged illness.

A rather large number of works is dedicated to the life, pedagogic, and scientific activity of V.A. Kistyakovskii.

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