

## HYDRATING IONS IN ST. PETERSBURG AND MOSCOW; IGNORING THEM IN LEIPZIG AND BALTIMORE

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### Debates over the “New” Physical Chemistry

The debates that swirled around the early development of modern physical chemistry in the late 19th century played themselves out in several different arenas: free ions vs. hydrates, dissociation vs. association, and, more broadly, physics vs. chemistry (1). But regardless of how any particular aspect of these debates was framed, the two sides were almost always seen as incompatible with each other. On one side were the “Three Musketeers of Physical Chemistry(2)” — Arrhenius, van’t Hoff, and Ostwald — and their numerous converts, many of whom were initiated into the physical theory of solutions, including dissociation and ions, in Ostwald’s lab in Leipzig (3). On the other side were the “three irreconcilables(4)” — Henry Armstrong, Louis Kahlenberg, and Isidor Traube — along with a few other holdouts, who could not bring themselves to believe that substances simply “fell apart” in solution and preferred a chemical view of association instead.

Because of the centrality of aqueous solutions in these debates, the role of water was crucial. The ionists regarded water as nothing more than an inert medium throughout which the dissociated ions of a dissolved electrolyte distribute themselves. Until the end of the 19th century, the ionists in Western Europe and America remained steadfast in their conviction that water and ions do not interact with each other, even with the increase in experimental results that seemed incompatible with a model of the solvent as an uninvolved bystander. The anti-ionists, though fewer in number, believed just as ardently that association, rather than dissociation, is the

process occurring in solution. Hydrate formation was seen as one way in which water and the dissolved substance could interact with each other, and Mendeleev’s hydrate theory (5) provided a rallying point for the anti-ionists, at least for a while.

This standoff over hydrates continued until after the turn of the century even though they had been mentioned nearly forty years earlier as a possible explanation for the anomalous results of freezing-point measurements on electrolyte solutions, first by Friedrich Rüdorff [1832-1902] in 1861 (6) and then by Louis de Coppet [1841-1911] ten years later (7). Although hydrates, as well as more general questions about the nature of solution, generated considerable discussion and debate throughout the latter part of the 19th century (8), the ionists’ unified front on this issue remained intact until the early years of the 20th century.

Beginning in 1900, Harry Clary Jones [1865-1916], Professor of Physical Chemistry at Johns Hopkins University, developed a solvate theory, which he regarded as compatible with dissociation theory. After a Ph.D. degree from Hopkins in 1892, he traveled to Europe as a postdoctoral student for two years, working with Ostwald, as well as with Arrhenius in Stockholm and van’t Hoff in Amsterdam. Probably the most ardent American ionist of his time, Jones proselytized vigorously on behalf of dissociation theory, with Ostwald describing him (9) as “one of my most loyal and devoted pupils.”

After returning to Baltimore in 1894, Jones continued his research on electrolytes and solution theory,

but he and his students could not explain certain freezing-point data (10):

...in terms of any relation that was then known. . . . Yet it seemed impossible to interpret the results obtained in terms of any other assumption than that a part of the water present was combined with the dissolved substance, and was therefore removed from playing the rôle of solvent. Accordingly, in 1900, the suggestion was ventured, for want of any better, that hydration in solution would explain these results.

Admittedly “antagonistic to any hydrate theory” (11) prior to his “suggestion . . . ventured, for want of any better,” Jones then spent more than a decade in developing his solvate theory of solutions. He reviewed the work by himself and his students in two long papers (12), as well as in several shorter summaries (13). While he still ignored previous work by Rüdorff and most others on the topic of hydration, Jones (14) specifically dismissed the earlier hydrate theory of Mendeleev as having no relevance or connection to his own. Referring to experiments that he had carried out in Arrhenius’ laboratory in Stockholm in 1893, Jones stated categorically that they showed “not the slightest evidence in favor of Mendeléeff’s theory of the existence of very complex hydrates in dilute solutions(15)”.

Jones characterized his theory as “radically different” from Mendeleev’s, which predicted the formation of “a few definite compounds with water,” such as  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \cdot 25 \text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 \cdot 100 \text{H}_2\text{O}$ . Jones believed that his own evidence for sulfuric acid and other electrolytes suggested the formation of “a complete series of hydrates with water, having all compositions ranging from one molecule of water up to at least thirty or forty molecules” (16), with “the amount of combined water for any given substance being a function of the concentration of the solution and of the temperature” (17). His theory encompassed all solvents, not just water, and he wrote (18):

Indeed, enough evidence has already been obtained to make it highly probable that solvation is not limited to aqueous solutions but is a general property of solutions. Solvents in general have more or less power to combine with substances dissolved in

them—in a word, *we have the solvate instead of simply a hydrate theory.*

However, a full decade before Jones reluctantly stopped ignoring the possibility of hydrated ions and embraced the concept of solvation, two Russian chemists, Ivan Alekseevich Kablukov [1857-1942] and Vladimir Aleksandrovich Kistiakovskii [1865-1952], independently suggested that hydration could—and *should*—be regarded as complementary, rather than contradictory, to dissociation. Both had been students of Mendeleev in St. Petersburg and also in Ostwald’s laboratory in Leipzig, where they studied with the original ionists. Neither of them assembled the extensive experimental basis for hydration that Jones did (19), but they certainly deserve recognition for their roles in the early improvements to Arrhenius’ original dissociation hypothesis (20). Kablukov and Kistiakovskii promoted the concept of hydrated ions long before Jones began his flirtation with them in 1900.

### Ivan Alekseevich Kablukov

Kablukov was born into the family of an emancipated serf in a small village near Moscow. At the age of eleven he began formal schooling at the Second Moscow Classical Gymnasium, from which he graduated in 1876. Later that year he entered Moscow University as a student in the Natural Science Section of the Physics and Mathematics Department. Kablukov recalled his university matriculation (21):

I remember that year when I became a student at Moscow University for the first time. I was very poor and wore an overcoat loaned to me by my brother, but it seemed to me that all of Moscow envied me. With pride, I repeated to myself: “I am a student at the university established by the great Lomonosov.”

It was not chemistry, however, that initially attracted Kablukov to science. He spent more than a year in the Zoological Museum until he “happened upon the chemistry laboratory at Moscow University at a time of enthusiasm for organic chemistry” (22). V. V. Markovnikov [1838-1904], who occupied the chair of organic chemistry at that time, must have seen the young student’s potential since he set him to work almost immediately on the synthesis of a glycerine derivative. Kablukov received his candidate’s de-



I. A. Kablukov as a student at Moscow University. Photo courtesy of LAFOKI, Russian Academy of Sciences.

gree from Moscow University in 1880, and the following year he was awarded a gold medal for his thesis, "Polyatomic Alcohols and Their Immediate Derivatives" (23).



An undated photograph of I. A. Kablukov. Photo courtesy of LAFOKI, Russian Academy of Sciences.

Markovnikov arranged for Kablukov to study with his own teacher, A.

M. Butlerov [1828-1886], at St. Petersburg University during 1881-1882. Besides attending Butlerov's lectures on organic chemistry, Kablukov also heard Mendeleev [1834-1907] lecture on inorganic chemistry and N. A. Menshutkin [1842-1907] on analytical chemistry and the history of chemistry. Kablukov later recalled that Mendeleev had awakened his interest in inorganic and (pre-Ostwaldian) physical chemistry. Although he again performed research under the direction of Markovnikov after his return to Moscow, he was also branching out beyond the boundaries of organic chemistry by teaching a practical course in quantitative analysis (24).

By 1887 when he defended his master's thesis, "Glycerines or Triatomic Alcohols and Their Derivatives," Kablukov had become a privat-docent and was teaching courses on physical and inorganic, as well as organic, chemistry. With the appearance of the new physical chemistry in 1887, Kablukov began offering a course entitled "On the Phenomena of Dissociation" (25). His increasing interest in applying physical methods of investigation to chemical problems led him to undertake research in the Physics Laboratory at Moscow University while still teaching chemistry.

In 1889 Kablukov arranged to spend three months in Ostwald's laboratory, where he worked under the direction of Arrhenius. His results on the electrical conductivity of HCl and H<sub>2</sub>SO<sub>4</sub> in various nonaqueous solvents showed—perhaps for the first time—that the relationship between the electrical conductivity and concentration of these electrolytes in alcohol solutions is the opposite of that in aqueous solutions (26). Kablukov

interpreted these results as suggesting some kind of solvent effect on the solute, though he apparently did not speculate on the exact nature of the effect.

Back in Moscow Kablukov continued this work on electrolyte solutions in the laboratory of A. P. Sabaneev [1843-1923], professor of analytical chemistry. Two years later he defended his doctoral dissertation (27), which was the first systematic discussion of the new physical chemistry in Russian. After presenting Arrhenius' picture of the breakup of an electrolyte into separate ions in aqueous solution, Kablukov wrote (28): "In our opinion, water does indeed decompose the molecules of the dissolved substance into separate ions, but in addition, these ions that are formed can combine with water into more complex groups .." He returned to this idea later in his dissertation (29):

[I]t is impossible to look at the solvent as a medium that is indifferent to the dissolved substance, and it is necessary to accept some kind of chemical interaction between the dissolved substance and the solvent.

In recalling this work many years later, Kablukov said that as a student of Mendeleev, he was unable to accept Arrhenius' idea that ions in solution do not interact in any way with the solvent (30). His dissertation concludes with the following observation (31):

Our investigations once more confirm that the solution of one substance in another should be regarded as a medium containing a mixture of different products from the chemical interaction between solute and solvent. Such a solution changes the physical and chemical properties of the solute, and all the properties of the solution depend on the strength of the interaction between solute and solvent. Our investigations into the "avidity" of acids show that this property is not a constant property of each acid, but depends on the nature of the solvent in which the acid is dissolved. And it depends not only on the nature of the solvent, but also on the relative amount of solvent, in other words, on the concentration of the solution. Referring to the viewpoint of Arrhenius, we can say that the "avidity" or "relative affinity" of an acid depends on its degree



An undated photograph of I. A. Kablukov. Photo courtesy of LAFOKI, Russian Academy of Sciences.

of dissociation, which can serve as a measure of the chemical interaction between the solute and solvent.

Thus, Kablukov contended that there is no inherent contradiction between ionic dissociation and ionic hydration, and in the 1902 edition of his *Basic Principles of Physical Chemistry*, he wrote that “in the forthcoming and more complete theory of solutions, both theories will merge” (32). This was exactly what Harry Jones was beginning to work toward about that time (33).

Amid the generally hostile reception of the new solution theory in Russia—though somewhat less in Moscow than in St. Petersburg—Kablukov voiced his ardent support in the debates among his university colleagues and members of the various scientific societies, as well as in the popular press (34). However, he never elaborated any specific merger of dissociation and hydration himself as his teaching positions and research interests led him to other areas of physical and inorganic chemistry, as well as to practical problems in industry and agriculture (35).

### Vladimir Aleksandrovich Kistiakovskii

Kistiakovskii's immediate family origins (36) were very different from those of Kablukov. He was born in Kiev in 1865, the son of a prominent academic and expert in criminal law, and he grew up in a household of intense intellectual activity. This also included science as a paternal uncle, a physician, had defended his doctoral dissertation in medical chemistry (37).

After graduating from the Second Kiev Gymnasium in 1883, Kistiakovskii entered the Physics and Mathematics Department at Kiev University, which celebrated the fiftieth anniversary of its founding the following year. During these celebrations student protests erupted against restrictive regulations and the low level of instruction. In response, officials closed the university and expelled the entire student body. Although students were readmitted the next fall, Kistiakovskii chose not to return. A year later he entered St. Petersburg University, where instruction in the physical and mathematical sciences was far superior to that in Kiev at the time.

In his first experimental work at St. Petersburg, Kistiakovskii studied the action of the acids of arsenic on alkenes under the supervision of M. D. L'vov [1848-1899], a former student of Butlerov. At the same time, however, Kistiakovskii was falling under the spell of the new physical chemistry emanating from Leipzig, and in December 1888 he gave Menshutkin an essay entitled

“The Planck-Arrhenius Hypothesis,” for which he received the candidate's degree the following year. This unpublished thesis was discovered only in the mid-1950s in the archives of the Academy of Sciences of the USSR (38).

Despite the general hostility of the St. Petersburg chemists toward dissociation theory, Menshutkin was sufficiently curious about the new physical chemistry from Leipzig to have a student examine it in detail (39). Kistiakovskii's thesis consists of three parts: a description of the theory of electrolytic solution, a critical analysis of the theory, and a detailed attempt to merge the concept of ions with Mendeleev's hydrate theory (40). Although this project began as a literature study, it became a vehicle for serious speculation by the 23-year-old Kistiakovskii. The young student did not regard the discrepancies between the theory and experimental data on strong electrolytes and concentrated solutions as the most serious flaw in Arrhenius' theory; rather, it was the refusal of the Ostwaldian camp to admit any kind of interaction between solute and solvent particles. To Kistiakovskii's way of thinking, such interaction was the only possible source of the energy needed for dissociation to occur (41).

Early in 1889 Kistiakovskii received the candidate's degree from the Physics and Mathematics Department at St. Petersburg University, and that spring he traveled to Leipzig for a year-long stay in Ostwald's laboratory. Kablukov was there at the time, and L'vov wrote to him (42):

His name is Kistiakovskii. . . . Please become acquainted with him. I am certain you will not regret it. In spite of the fact that he has been doing serious study for only about a year or less, you will find in him good stuff and a continual tendency to independent speculation, sometimes very original and ingenious. Frankly speaking, I will be sad if he gets bogged down with ions.

These must have been heady days for Kistiakovskii, as they were for many young chemistry students from Europe and America, toiling on the Mt. Olympus of the Leipzig laboratory with the gods themselves of the new physical chemistry. Kistiakovskii worked on an experimental problem concerning the ionic nature of double salts, but the young Russian also engaged in theoretical discussions with Arrhenius, Ostwald, Nernst, and others. He argued that ions must interact with the surrounding solvent molecules. Kistiakovskii recalled one such debate in which he said that “it was difficult to understand the existence of free (unhydrated) ions in water.”

Ostwald replied, "You will agree that if it is difficult to understand, then it was even more difficult to discover" (43).

The 1890 paper (44) describing Kistiakovskii's investigation of double salts concludes with a section entitled "Specific Attractions in Salt Solutions." In it he undertakes a theoretical analysis of solute-solvent interactions in terms of van der Waals forces between an ion and the water molecules within its sphere of influence. Kistiakovskii specifically examines the freezing of an electrolyte solution—the very anomaly that later drove Jones to embrace hydrates—on the basis of the principle of least work. His results suggested that salt solutions contain complexes of ions and water molecules. Writing about this period in his life, Kistiakovskii remarked that although it was extremely gratifying to have been heading in the right direction in connection with ionic hydration, it grieved him that he had never been able to convince his friend Arrhenius of the relevance of Mendeleev's hydrate theory to ions (45). But curiously, even when Jones, who had worked with Arrhenius, became convinced of the relevance of solvates to electrolytes in solution, he never referred to this paper by Kistiakovskii. While it would be understandable that Jones was unaware of Kablukov's dissertation, which was not translated from Russian into any other language, it seems implausible that he could have been unaware of a paper written in German and appearing in *Zeitschrift für physikalische Chemie*.

Kistiakovskii returned to St. Petersburg in November, 1890. Even though the attitude toward the new physical chemistry was far more conservative and critical there than it was for Kablukov in Moscow, Menshutkin formally requested the chemistry faculty to admit Kistiakovskii to prepare for the examination for the master's degree. After a year without financial support, Kistiakovskii requested a stipend, which was denied in spite of a faculty report of his "excellent accomplishments." He worked a second year with no financial support and passed his master's examination in 1892. After a third such year Kistiakovskii took a position in the government's Department of Trade and Manufacture, became a regular contributor to several popular science magazines, and began teaching physics at the St. Petersburg Women's Gymnasium (46).

In 1896 Kistiakovskii became a privat-docent at St. Petersburg University, offering the courses "Chemical Transformations" and "Nernst's Theory of Diffusion." Also that year he presented his master's thesis, "Chemical Transformation in a Homogeneous Medium at Constant Temperature," a kinetic study of ether formation, but he was not given the opportunity to defend it. The committee of three chemists and a mathematician (47) rejected the thesis as unsuitable for a degree in chemistry. They objected to the focus on mathematical equations and the calculation of rate constants. While admitting that the thesis did "touch on the very interesting and much discussed problem of the reasons for the specific influence of an acid on the formation and decomposition of complex ethers," the committee concluded that Kistiakovskii had not only failed to advance a solution to this problem, but had actually pushed the problem aside. Their decision stated that the thesis contained nothing new, original, or worthy of their attention (48).



An undated photograph of V. A. Kistiakovskii. Photo courtesy of LAFOKI, Russian Academy of Sciences.

In spite of this setback, Kistiakovskii continued his experimental investigations in the physics laboratory at the university. In January, 1898 he accepted a temporary appointment as laboratory assistant in chemistry, while still offering courses, including new ones in physical chemistry and electrochemistry. Over the next several years he gave up his other positions in order to spend more time on his research, apparently still with the hope of receiving a permanent place at the university. At the same time, however, he continued as an active proponent of the new physical chemistry (49). In 1901 he was invited to deliver the paper "An Analysis of the Objections to the Theory of Electrolytic Dissociation" to the Eleventh Congress of the Russian Chemical Society (50). While Kistiakovskii managed to find some allies in this area, particularly outside St. Petersburg, his advocacy of the new physical chemistry effectively excluded him from a permanent position at the university (51).

This difficult and uncertain period in his life finally came to an end in 1902 when he became laboratory assistant in chemistry at the newly created Polytechnic Institute in St. Petersburg. The following year Kistiakovskii wrote a second master's thesis, "Physicochemical Investigations"—which contained his earlier work on ethers, as well as additional work on the elec-

trochemistry of double salts and the determination of molecular weights of liquids—and submitted it, not in St. Petersburg, but to Moscow University (52). After receiving the degree, he became Professor of Chemistry at the Polytechnic Institute, where he set up the first independent laboratory of physical chemistry and electrochemistry in Russia (53).

Because of the applied nature of the education offered at the Polytechnic Institute, Kistiakovskii's research became more directed toward practical problems in electrochemistry and metallurgy. In 1910 he successfully defended his dissertation "Electrochemical Reactions and Electrode Potentials of Various Metals" for the degree of Doctor of Chemical Sciences, also at Moscow University (54). Kistiakovskii became an important figure in the development of the Russian and Soviet physical chemistry and electrochemistry. He was a member of the Academy of Sciences of the USSR, and in 1930 he organized a laboratory of colloid electrochemistry, which became an institute of the Academy of Sciences of the USSR in 1934 (55).

### Conclusion

As students in Leipzig, Kablukov and Kistiakovskii came from a scientific culture that was still moving to catch up with that of Western Europe. Original research was not a significant part of the professional life of Russian chemists before the 1860s (56). In 1861, for example, a letter from Academician C. J. Fritzsche [1808-1871] to the young Mendeleev demonstrates the attitude of at least one older Russian chemist (57):

I received a shallow education—not the sort you received. . . . I do not have the strength to catch up with you. . . . I respect, with my whole soul I respect your views, your direction. Your theoretical frame of mind sometimes is incomprehensible to me.

This transformation of Russian science to the Western research model was still incomplete in the 1870s and 1880s when Kablukov and Kistiakovskii were students.

In their student days at St. Petersburg, Kablukov and Kistiakovskii were immersed in a scientific culture in which there already was a "physical" chemistry predating the new physical chemistry that originated in Leipzig in the latter 1880s. Among Mendeleev's many interests was the application of physical methods to the study of chemical systems, and it was his density measurements on solutions over wide concentration ranges that lent support to his hydrate theory (58). Interestingly, the students from Russia brought definite ideas

about the nature of solutions with them to Leipzig, but the ideas that Kablukov and Kistiakovskii brought were not ones that appealed to the ionists. The physical theory of solution was sufficiently successful in the limited domain of dilute aqueous solutions that its proponents felt little need to re-examine their rejection of solute-solvent interactions.

In spite of their background—or because of it—students from the Russian chemical tradition would undoubtedly be seen as having inferior training in comparison to students from the West. This attitude about Russians undoubtedly extended even to Kablukov, who had spent nearly twelve years as a student of chemistry at Moscow and St. Petersburg universities before going to Ostwald's laboratory. Kablukov had considerably more experience in the study and teaching of chemistry than the typical student from the West, and he was actually two years older than Arrhenius [1859-1927] and only 4-5 years younger than Ostwald [1853-1932] and van't Hoff [1852-1911]. Nor was returning to Russia from Leipzig necessarily the end of their status as outsiders, though the ease of their reintegration into the Russian chemical community seems to have been directly proportional to their distance from St. Petersburg, the epicenter of Mendeleev's influence. In Moscow Kablukov fared rather well—he was also older and more experienced than Kistiakovskii—and he was able to use the new physical chemistry as the basis of his successful doctoral dissertation (59). Kistiakovskii was far less successful in St. Petersburg. Not only was he unable to obtain any further degrees there, but his continued advocacy of the new physical chemistry ultimately kept him from an academic appointment at the university.

As students, Kablukov and Kistiakovskii were caught between the new physical chemistry of Leipzig, which intrigued them, and the older physical chemistry of St. Petersburg, which helped mold them, but then hindered them—though to different degrees—in their subsequent careers in Russia. In Leipzig there were ions, but no hydrates; in St. Petersburg there were hydrates, but few ions. The academic niches they were able to find beyond the direct influence of St. Petersburg University enabled them to work in areas of research that capitalized on the new ideas about electrolyte solutions, but did not directly involve the fundamental issues that still needed to be resolved in order to bring dissociation theory into better agreement with experimental observations. While Harry Jones was apparently unable to accept the limited role of solvate theory in explaining the anomalies of electrolyte behavior (57), Kablukov

and Kistiakovskii spent many productive years in solving more applied problems in physical chemistry and electrochemistry and making important contributions to the development of these fields of research in Russia and the Soviet Union.

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- p 175) states that this "idea of Rüdorff [about hydration] was carried out on a large scale by H. C. Jones and his pupils, with due regard to the dissociation."
15. Ref. 9, Jones, pp 46-48; Ref. 14, p 249.
  16. Ref. 14, p 249.
  17. Ref. 9, Jones, p 349.
  18. Ref. 9, Jones, p 350.
  19. Jones and his students gathered a tremendous amount of experimental data on solutions, much of which was published by the Carnegie Institution of Washington in ten reports from 1907 to 1915. These reports are cited in Ref. 9, Jones, pp 368-369. For the generally unfavorable reaction of many of Jones' colleagues to his solvate theory, see Ref. 3, pp 75-78.
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  22. Ref. 21, p 181.
  23. Iu. I. Solov'ev, M. I. Kablukova, and E. V. Kolesnikov, *Ivan Alekseevich Kablukov: 100 Let so Dnia Rozhdeniia, 1857-1957 [Ivan Alekseevich Kablukov: 100 Years from His Day of Birth, 1857-1957]*, Izd. Akademii Nauk SSSR, Moscow, 1957, 27-28.
  24. Ref. 23, pp 28-34.
  25. V. A. Polosin, and N. M. Nesterovaia, *Ivan Alekseevich Kablukov*, Izd. Akademii Nauk SSSR, Moscow, 1957, 9; Ref. 23, pp 34-35.
  26. I. Kablukoff, "Über die elektrische Leitfähigkeit von Chlorwasserstoff in verschiedenen Lösungsmitteln," *Z. Phys. Chem.*, **1889**, *4*, 429-434.
  27. I. Kablukov, *Sovremennye Teorii Rastvorov (Fant-Goffa i Arreniusa) v Sviazi s Ucheniiami o Khimicheskoi Ravnovesii [The Modern Theories of Solution (of van't Hoff and Arrhenius) in Connection with Studies of Chemical Equilibrium]*, M. P. Shchepkin, Moscow, 1891.
  28. Ref. 27, pp 85-86.
  29. Ref. 27, p 134.
  30. I. A. Kablukov, "Istoricheskii Obzor Razvitiia Ucheniia o Nevodnykh Rastvorakh" ["Historical Survey of the Development of the Study of Nonaqueous Solutions"], in *Sbornik Trudov Pervoi Vsesoiuznoi Konferentsii po Nevodnym Rastvoram [Proceedings of the First All-Union Conference on Nonaqueous Solutions]*, Izd. Ukrainskoi Akademii Nauk, Kiev, 1935, 13-28 (17). Quoted in English by K. M. Gorbunova, L. J. Antropov, Iu. I. Solov'ev, and J. P. Stradins, "Early Electrochemistry in the USSR," in G. Dubpernell and J. H. Westbrook, Ed., *Selected Topics in the History of Electrochemistry*, Electrochemical Society, Princeton, NJ, 1977, 226-256 (235).
  31. Ref. 27, p 215.
  32. Ref. 30, Gorbunova *et al.*, p 237.
  33. Jones eventually reached the same conclusion as Kablukov. "The solvate theory of solution has been regarded in some cases as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not the case at all. The solvate theory begins where the theory of electrolytic dissociation ends. . . . The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution." See Ref. 13, *Chem. News*, p 126.
  34. I. Kablukov, "Sovremennaiia Teoriia Rastvorov" ["The Modern Theory of Solutions"], *Russkaia Mysl'*, **1891**, bk. 2, 208-228.
  35. Ref. 21, p 183.
  36. In anticipation of the inevitable question—yes, Vladimir Aleksandrovich Kistiakovskii and George Kistiakowsky [1900-1982] were, in fact, related. They were uncle and nephew. Vladimir Aleksandrovich's brother, Bogdan Aleksandrovich Kistiakovskii [1868-1920], was George Kistiakowsky's father. Trained in philosophy, Bogdan Aleksandrovich devoted his life to the law and sociology of the law and was a passionate advocate of "individual rights and democratic political institutions." See S. Heuman, *Kistiakovskii: The Struggle for National and Constitutional Rights in the Last Years of Tsarism*, Harvard University Press, Cambridge, MA, 1998, 1-38.
  37. The details of Kistiakovskii's early life are from N. A. Figurovskii and Iu. I. Roman'kov, *Vladimir Aleksandrovich Kistiakovskii*, Nauka, Moscow, 1967, 7-25.
  38. Ref. 37, pp 17-20; K. M. Gorbunova, "Akademik Vladimir Aleksandrovich Kistiakovskii, Nekrolog" ["Academician Vladimir Aleksandrovich Kistiakovskii, Obituary"], *Zh. Fiz. Khim.*, **1952**, *26*, 1717-1720 (1717); and Iu. I. Solov'ev, "O Neopublikovannoi Robote V. A. Kistiakovskogo 'Gipoteza Planka-Arreniusa'" ["On V. A. Kistiakovskii's Unpublished Work 'The Planck-Arrhenius Hypothesis'"], *Zh. Fiz. Khim.*, **1956**, *30*, 1910-1915. Kistiakovskii's dissertation is in the Archives of the Russian Academy of Sciences, fond 610, opis' 5, No. 1.
  39. Ref. 38, Solov'ev, p 1910.
  40. Ref. 37, pp 20-23.
  41. Ref. 38, Solov'ev, p 1912.
  42. Ref. 37, pp 26-27.
  43. Ref. 37, p 30; Ref. 38, Solov'ev, p 1914.



44. W. Kistiakowsky, "Die wässrigen Lösungen von Doppelsalzen," *Z. Phys. Chem.*, **1890**, 6, 97-121 (115-121).
45. V. A. Kistiakovskii, "Teoriia Elektroliticheskoi Dissotsiatsii Arreniusa i Evoliutsii Sovremennoi Khimii" ["The Theory of Electrolytic Dissociation of Arrhenius and the Evolution of Modern Chemistry"], *Trudy Komissii po Istorii Znaniia [Proceedings of the Commission on the History of Knowledge]*, Izd. Akademii Nauk SSSR, Leningrad, 1929. Quoted in Ref. 37, p 30.
46. Ref. 37, pp 34-36.
47. The committee consisted of the chemists D. P. Konovalov, N. A. Menshutkin, and A. E. Favorskii and the mathematician K. A. Posse. See Ref. 37, pp 37-38.
48. Ref. 37, pp 36-40.
49. V. A. Kistiakovskii, "K Teorii Rastvorov Vant-Goffa-Arreniusa" ["On the van't Hoff-Arrhenius Theory of Solutions"], *Zh. Russ. Fiz.-Khim. Obshch., Chast' Khim.*, **1897**, 29, sect. 1, pt. 4, 286-287; V. A. Kistiakovskii, "Desiatiletie Teorii Elektroliticheskoi Dissotsiatsii" ["Tenth Anniversary of the Theory of Electrolytic Dissociation"], *Elektrotekh. Vestn.*, **1898**, \_ 55, 313-316, \_ 56, 349-354; V. A. Kistiakovskii, "K Ucheniiu o Rastvorakh" ["On the Study of Solutions"], *Zh. Russ. Fiz.-Khim., Chast' Fiz.*, **1898**, 30, sect. 1, pt. 6, 576-585. See A. F. Kapustinskii, *Ocherki po Istorii Neorganicheskoi i Fizicheskoi Khimii v Rossii ot Lomonosova do Velikoi Oktiabrskoi Sotsialisticheskoi Revoliutsii [Essays in the History of Inorganic and Physical Chemistry in Russia from Lomonosov to the Great October Socialist Revolution]*, Izd. Akademii Nauk SSSR, Moscow/Leningrad, 1949, 140.
50. V. A. Kistiakovskii, "Razbor Vozrazhenii na Teoriiu Elektroliticheskoi Dissotsiatsii" ["An Analysis of the Objections to the Theory of Electrolytic Dissociation"], *Zh. Russ. Fiz.-Khim. Obshch.*, **1902**, 34, sect. 2, pt. 1, 19-33.
51. Ref. 37, pp 40-42.
52. Ref. 37, pp 50-59.
53. A. N. Frumkin, "Zhizn' i Nauchnaia Deiatel'nost' Akademika Vladimira Aleksandrovicha Kistiakovskogo" ["The Life and Scientific Activity of Academician Vladimir Aleksandrovich Kistiakovskii"], *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1946**, No. 2, 121-125 (121).
54. N. D. Dankov, *Vladimir Aleksandrovich Kistiakovskii*, Izd. Akademii Nauk SSSR, Moscow, 1948, 8.
55. Ref. 37, pp 111-115; Ref. 53, p 121.
56. N. M. Brooks, *The Formation of a Community of Chemists in Russia: 1700-1870*, Ph.D. Thesis, Columbia University, 1989, Ch. 6.
57. L. R. Graham, *Science in Russia and the Soviet Union: A Short History*, Cambridge University Press, Cambridge, 1993, 225.
58. Ref. 5, *Rastvory*, pp 381-1073, reprints Mendeleev's 1887 monograph, *Issledovanie Vodnykh Rastvorov po Udel'nomu Vesu [An Investigation of Aqueous Solutions by Means of Specific Gravity]*.
59. Ref. 23.
60. Ref. 9, Goldsmith, p 199.

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