The Life and Work of Nikolaĭ Semenovich Kurnakov

A FOUNDER OF THE RUSSIAN PLATINUM INDUSTRY

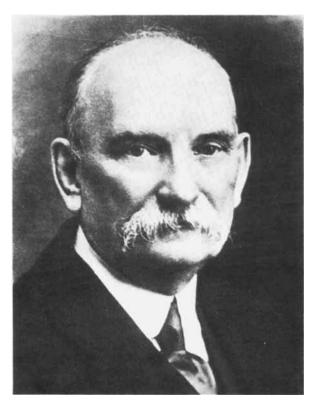
By Professor George B. Kauffman

California State University, Fresno, U.S.A.

For more than six decades, Nikolai Semenovich Kurnakov, one of Russia's most distinguished and versatile chemists, was an active force in the development of science and technology both in his homeland and abroad. He is regarded as the founder of a new chemical discipline, physicochemical analysis, probably the largest contemporary school of Soviet chemistry with applications in numerous branches of technology (1–23).

A beloved teacher as well as a creative theorist and experimentalist of the first rank,

Kurnakov organised and served as director of a number of laboratories, research institutes, and national and international commissions. He was largely responsible for the construction of several new chemical, mining, and metallurgical plants and was a pioneer in the systematic exploitation of Russian mineral resources, especially platinum, potassium, and magnesium. His more than 200 published articles and texts testify to his immense productivity in the widely-scattered fields of mineralogy, metallurgy, metallography, and



Nikolaĭ Semenovich Kurnakov 1860–1941

This internationally recognised scientist, regarded as the originator of physicochemical analysis, was one of the principal founders of the platinum industry in the U.S.S.R. His discovery of the reaction still used to differentiate cis from trans isomers of divalent platinum is his best-known contribution to co-ordination chemistry

Photograph by courtesy of the late Academician I. I. Chernyaev

salt technology, and inorganic, analytical, organic and physical chemistry. Through his active participation in scientific, public and governmental affairs, he became a public figure and a recipient of numerous honours.

Nikolai Semenovich Kurnakov was born in Nolinsk, Vyatka province, on December 6, 1860. From 1871 to 1877 he received the equivalent of a high school education at Gorki, and following this he entered the Saint Petersburg Mining Institute where independent research under chemists Sushin and Lisenko and mineralogist Yeremyev resulted in his first publication, a crystallographic study of alum and Schlippe's salt (Na₃SbS₄.9H₂O). After graduation in 1882, with the degree of Mining Engineer, he was retained by the chemical laboratory of the institute.

Kurnakov's interest in chemical industry would not permit him to remain exclusively a laboratory worker, and he now began the first of his many trips to plants, factories, smelting operations and laboratories. A detailed study of salt manufacturing in Prussia, Lorraine, Württemberg, Baden, Bavaria and the Austrian Tyrol, made in the summer of 1884, resulted the following year in his dissertation for the position of Assistant in metallurgy, halurgy (salt technology), and assaying, a post which he held for eight years. This work, "Evaporative Systems of Salt Boilers", containing the germs of Kurnakov's subsequent studies of salt equilibria, appeared long before van't Hoff's research on the Stassfurt salt beds.

Kurnakov's Reaction

In 1893 Kurnakov was appointed Professor of Inorganic Chemistry following the successful presentation of his dissertation "On Complex Metallic Bases", in which he described the reaction of Pt(II) and Pd(II) isomers with thiourea, now known as Kurnakov's reaction (24). In 1899 he was appointed Professor of Analytical Chemistry at the Mining Institute and organised the teaching of physical chemistry at the Saint Petersburg Electrotechnical Institute, where he taught until 1908. In 1902 he was appointed Professor of General Chemistry at

the Saint Petersburg Polytechnic Institute, which he had organised together with Mendeleev and Menschutkin, and he held this post until 1930.

During the first decade of the 20th century, Kurnakov was concerned with the solution of industrial problems such as platinum refining, metallic alloys, metallography, and salt manufacturing, and he played a vital role in the planning and construction of new laboratories at the three institutes.

In 1909 Kurnakov was awarded the degree of Doctor of Chemical Sciences honoris causa by Moscow University, became a contributing editor of the Zeitschrift für anorganische Chemie, and was appointed a member of the Mining and Scientific Committee. In 1910 he directed studies of the Russian Council on Platinum Refining, and the following year he went abroad to study methods of transporting warm sulphur waters.

Official recognition abroad followed recognition at home. In 1912 Kurnakov was elected a council member in the Société Chimique and became a member of the Russian Department of the International Commission on the Nomenclature of Inorganic Compounds. As a delegate of the Russian Physical-Chemical Society, he participated in the meetings of the International Association of Chemical Societies held at Berlin (1912) and Brussels (1913). In 1913 he was elected vice-president of the Russian Metallurgical Society and became Ordinary Academician in chemistry at the Akademiia Nauk (Academy of Sciences). The laboratory of the academy had been inactive for a number of years, but it experienced a rebirth as a result of Kurnakov's extraordinary organisational talent.

The difficult years of World War I and the period following it brought many new tasks for Kurnakov. He was instrumental in the creation of a number of new institutes and commissions. In 1915, together with fellow academicians V. I. Vernadskii and A. E. Fersman, he organised and became assistant chairman of the Commission for the Study of Russian Natural Productive Sources (K.E.P.S.) at the Academy. Here he

established a Salt Commission, and the study of salt solutions and related problems occupied much of his time for the next few years.

In 1919 he organised and became director of the State Institute of Applied Chemistry, a position held until 1927, with facilities located at Vasil'yevskii Island on the Neva at Petrograd, which had grown out of the first Russian laboratory founded by Mikhail Vasil'yevich Lomonosov (1711–1765). Here scientific workers from the provinces gathered, especially during the summers, to work under Kurnakov's guidance. They then returned home with ideas and projects for the next few years, and in this manner Kurnakov disseminated his ideas and expanded his rapidly growing school.

Institute for Study of Platinum

In 1918 at K.E.P.S., Kurnakov founded and became director of the initially-small Institute of Physicochemical Analysis, and the following year he became editor of its journal Izvestiya Instituta Fiziko-Khimicheskogo Analiza (now Izvestiya Sektora Fiziko-Khimicheskogo Analiza); he held both positions until his death. The year 1922 saw Kurnakov become director of the General Chemistry Laboratory of the Academy and, upon the death of Lev Aleksandrovich Chugaev, director of the Institute for Study of Platinum and Other Noble Metals, and a member of the Göttingen Akademie (25).

In 1934 the Institute of Physicochemical Analysis, the Platinum Institute, and the General Chemistry Laboratory of the Academy merged into the Institute of General and Inorganic Chemistry with headquarters in Moscow and with Kurnakov as its director. This rapidly became one of the leading scientific research institutes in the U.S.S.R. and a centre for physicochemical investigations of metallurgy, halurgy, noble metals, organic substances, and other economically-significant problems (26). Following Kurnakov's death in 1941, it was renamed the N. S. Kurnakov Institute, and it has continued in the tradition of its founder.

From 1920 to the end of his life there were few chemical or metallurgical conferences in which Kurnakov failed to participate as chairman, lecturer, or delegate. He was chairman of the Chemical Association of the Academy of Sciences of the U.S.S.R. (1930 to 1938), vice-president of the D. I. Mendeleev All-Union Society, and in 1939 to 1940 chairman of the society's All-Union Competition Jury for the selection of the best scientific research works. In addition to his industrial consulting, in which he gave technical advice to plants and factories throughout the U.S.S.R., Kurnakov was extremely active in public affairs.

Kurnakov's contributions acknowledged on numerous occasions by high awards from the Soviet government, including one to recognise the fourth edition of his book "Vvedenie v Fiziko-Khimicheskii Analiz" (Introduction to Physicochemical Analysis) (27), which was dedicated to the memory of his closest friend, his wife Anna Mikhailovna, who for more than half a century had accompanied him everywhere and supported him in all his endeavours. In 1951 Kurnakov's portrait appeared on a postage stamp, part of a commemorative issue honouring Mendeleev, Butlerov, Lobachevskii, Kalinnikov, and other outstanding figures of Russian art and science.

His wife's death in 1940 had serious effects on Kurnakov's health. Ignoring the cancer which was soon to claim his life, he continued his full work schedule almost to the very end, and when his colleagues enquired as to the state of his health, which was visibly deteriorating, he quickly shifted the conversation to scientific topics. At the beginning of March, 1941 he entered the sanatorium at Barvikha where he died on March 19th. Although a scientist of international reputation, he remained a modest and considerate person, approachable to colleagues and students alike.

The Kurnakovs had two children—a son Dr. Nikolai Nikolaevich Kurnakov (born in 1889), a chemist who worked at the Baikov Metallurgical Institute of the Academy of Sciences of the U.S.S.R., and a daughter Vera Nikolaevna Kurnakov (born in 1898), who died at the age of 23 while still a student. Kurnakov's work is continued by an extensive

school of scientists armed with new research methods, new apparatus, new theories, and new applications which he himself had created.

Kurnakov's Work on Co-ordination Compounds

Kurnakov's studies of complex compounds (1, 16, 17, 19), carried out largely during the years 1891 to 1902 and following closely upon his early works on halurgy, constitute his first mature research. Two factors attracted Kurnakov to the field of platinum complexes his interest in Russian natural resources and the then current controversy between the widelyaccepted Blomstrand-Jørgensen chain theory and the revolutionary Werner co-ordination theory (28). While not completely accepting or rejecting either theory, Kurnakov regarded complexes as intermediate between chemical compounds of fixed composition and phases of varying composition (29), a harbinger of his later (1914) "berthollide-daltonide" dichotomy.

Kurnakov did not limit himself to the synthesis of new complexes, but he investigated and sought relationships between a number of their physical and chemical properties, a search which eventually led him to the development of physicochemical analysis. His analogy between complex ions and simple metallic ions was subsequently developed by Chugaev and his school, investigation while Kurnakov's of relationship between acid-base properties of complexes and their solubilities (30), opened an area later explored more fully by A. A. Grinberg and co-workers. Kurnakov's study of refractive indexes is still of importance in connection with dipoles. His use of colour as a means of investigating complex species in solution (31) was later continued by Niels Bjerrum in his elucidation of the composition of chromium complexes.

In 1893, the year of the publication of Werner's co-ordination theory, Kurnakov observed an important regularity in the substitution reactions of co-ordination compounds. Chemical reactions permitting a distinction between inorganic geometric isomers are unfortunately all too rare, and Kurnakov's

discovery of a reaction still used to differentiate cis from trans isomers of divalent platinum or palladium undoubtedly represents his most widely-known contribution to co-ordination chemistry (24). While investigating the substitution of ligands by thiourea and thioacetamide, Kurnakov found that replacement occurred with all the ligands of the cis compound, but only with acid radicals of the trans compound:

$$(cis) \qquad \begin{bmatrix} A & X \\ Pt \\ A & X \end{bmatrix} + 4tu \rightarrow \begin{bmatrix} tu & tu \\ Pt \\ tu & tu \end{bmatrix} X_2 + 2A$$

$$(trans)\begin{bmatrix} \overline{A} & \overline{X} \\ Pt \\ X & A \end{bmatrix} + 2tu \longrightarrow \begin{bmatrix} \overline{A} & t\overline{u} \\ Pt \\ t\overline{u} & A \end{bmatrix} X_2$$

where $A = NH_3$ or an amine; X = halogen or acid radical; tu = thiourea). Kurnakov's classic reaction later played a crucial role in Werner's proof of the square planar configuration of Pt(II) and in the formulation of Il'ya Il'ich Chernyaev's trans effect (32).

Kurnakov is regarded as one of the principal founders of the platinum industry of the U.S.S.R. Although platinum had been and continues to be one of that vast country's most valuable natural resources, prior to the work of Kurnakov and his colleagues Russia was forced to export raw platinum abroad and to import the refined metal because refining methods were kept secret by foreign refining companies. With the nationalisation of the Russian platinum industry following the Bolshevik Revolution of 1917, it became necessary to organise the refining of all the metals of the platinum group within the U.S.S.R. Industrial organisations in the Urals turned to Kurnakov, who, as Chairman of the Refining Council of the Platinum Institute of the Academy of Sciences, accomplished the task in co-operation with factory workers. By 1930 all six platinum metals were being successfully produced in great purity within the U.S.S.R. (17, 21).

While directing the Institute of General and Inorganic Chemistry, Kurnakov did much to facilitate the development of co-ordination theory and the application of complexes to the refining of the platinum metals. In Kurnakov's laboratory at the Leningrad Mining Institute, his co-workers N. I. Podkopaev and N. N. Baraboshkin developed methods for refining raw platinum which were later realised on a larger scale at the Sverdlovsk Refinery, thus making the U.S.S.R. independent of other nations for its refining of platinum (16, 33).

The two-volume "Collection of the Selected Works of N. S. Kurnakov" (34), issued in 1938-39, contains a complete list of his

research published up to that time. Although one must allow for the inevitable overvaluation found in the Russian articles which were an important source of information for this paper, the majority of Kurnakov's works, even those published as much as a half century ago, are still of great theoretical and practical interest.

Acknowledgements

The author wishes to acknowledge the assistance of the late Academician Il'ya I. Chernyaev, who graciously provided information, reprints, and the photograph which appears in this article. The present study resulted from interest in Kurnakov aroused by a research project on the separation of inorganic geometric isomers sponsored by the Research Corporation and the National Science Foundation (NSF G-I124I).

References

- I G. G. Urazov and V. Nikolaeva, Uspekhi Khim., 1939, 8, (6), 785
- 2 S. I. Vol'fkovich. Uspekhi Khim., 1941, 10, (7), 757
- 3 G. G. Urazov, Uspekhi Khim., 1952, 21, (9), 1019
- 4 S. A. Pogodin, Uspekhi Khim., 1952, 21, (9), 1034
- 5 I. I. Kornilov, Uspekhi Khim., 1952, 21, (9), 1045
- 6 V. K. Semenchenko, *Uspekhi Khim.*, 1952, 21, (9), 1068
- 7 I.N. Lepeshkov, Uspekhi Khim., 1952, 21, (9), 1079
- 8 N. K. Voskresenskaya, *Uspekhi Khim.*, 1952, 21, (9), 1086
- 9 L. S. Dlugach, Zavodskaya Lab., 1941, 10, 109
- 10 N. N. Efremov, Bull. Acad. Sci., U.R.S.S., Classe Sci. Chim., 1941, 449
- 11 N. K. Voskresenskaya, Zh. Priklad. Khim. (Leningrad), 1941, 14, (6), 711
- 12 J. Chem. Ind. (U.S.S.R.), 1941, 18, 1
- 13 J. Chem. Ind. (U.S.S.R.), 1941, 18, 58
- 14 A.F.Kapustinskii, Zh.Fiz.Khim., 1941,15,(4),417
- 15 N. K. Voskresenskaya, Zh. Fiz. Khim., 1960, 34, (12), 2625
- 16 I. I. Chernyaev, Izwest. Sektora Platiny i Drugikh Blagorodnykh Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R., 1948, 21, 7
- 17 O. E. Zvyagintsev, Izvest. Sektora Platiny i Drugikh Blagorodnykh Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R., 1954, 28, 133
- 18 V. Ya. Anosov, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R., 1946, 14, 37
- 19 N. N. Efremov, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei 1 Neorg. Khim., Akad. Nauk S.S.S.R., 1946, 14, 63
- 20 G. G. Urazov, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R., 1941, 14, 9

- 21 O. E. Zvyagintsev, Zh. Neorg. Khim., 1957, 2, (10), 2281
- 22 S.Z.Makarov, Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk, 1960, (12), 2073; A. S. Berezhnoi, Ukrain. Khim. Zh. 1960, 26, (6), 684; O. E. Zvyagintsev, Zh. Priklad. Khim. (Leningrad), 1960, 33, (10), 2385; M. A. Klochko, Zh. Obshchei Khim., 1960, 30, (11), 3509; "Nikolai Semenovich Kurnakov v vospominaniyakh savremennikov i uchenikov", Akad. Nauk S.S.S.R., Moskva, 1961; Yu. I. Solov'ev and O. E. Zvyagintsev, "Nikolai Semenovich Kurnakov", Izdatel'stvo Akad. Nauk S.S.S.R., Moskva, 1960
- 23 G. B. Kauffman and A. Beck, J. Chem. Educ., 1962, 39, (1), 44
- 24 N. S. Kurnakov, J. Russ. Phys. Chem. Soc., 1893, 25, 565, 693; J. Prakt. Chem., 1894, 50, (11-12), 481
- G. B. Kauffman, Platinum Metals Rev., 1973, 17,
 (4), 144; ibid., 1974, 18, (4), 142
- 26 N.S. Kurnakov, Uspekhi Khim., 1936, 5, (7-8), 957
- 27 N. S. Kurnakov, "Vvedenie v Fiziko-Khimicheskii Analiz", 4-e lzd., Akad. Nauk S.S.S.R., Moskva, 1940
- 28 G. B. Kauffman, J. Chem. Educ., 1959, 36, (10), 521; Chymia, 1960, 6, 180
- 29 N. S. Kurnakov, J. Prakt. Chem., 1895, 52, (4), 177; ibid., 1895, 52, (10–11), 490
- N. S. Kurnakov, J. Russ. Phys. Chem. Soc., 1892, 24, 629
- 31 N. S. Kurnakov, Z. Anorg. Chem., 1898, 17, 207
- 32 G. B. Kauffman, Platinum Metals Rev., 1976, 20, (4), 126
- 33 N. S. Kurnakov et al., Ann Inst. Platine, 1932, 9,
- 34 "Sobranie Izbrannykh Rabot N. S. Kurnakova", 2 vols., Moskva, Leningrad, 1938–39