The Discovery of Ruthenium

"I NAMED THE NEW BODY, IN HONOUR OF MY MOTHERLAND"

By V. N. Pitchkov
Moscow Academy of Fine Chemical Technology, Russia

In 1844 Karl Karlovitch Klaus, then an unknown professor at the University of Kazan, reported his discovery of a new platinum metal which he named ruthenium, after Ruthenia, the latinised name for Russia. Besides studying the characteristics of ruthenium, Klaus conducted a wide ranging investigation of rhodium, iridium, osmium, and to a lesser extent, palladium and platinum. Thus, he may be regarded as the creator of the chemistry of the platinum metals, and the one who introduced the concept of the structure of the “double salts and bases” of platinum, which was developed some forty years later by Alfred Werner in his co-ordination theory. Klaus also discovered the similarities and differences between elements in the triads: ruthenium-rhodium-palladium and osmium-iridium-platinum, so providing the justification for Dmitri Ivanovich Mendeleev to include all six platinum metals in Group VIII of the Periodic System. Klaus’s work thus marked an epoch in the investigation of the platinum metals, especially of ruthenium— the last one to be discovered.

Karl Karlovitch Klaus was born on January 11th, 1796 at Dorpat in what was then Russia (now known as Tartu, in Estonia). When he was four years old his father died, and the following year his mother, after a second marriage to another artist, also died, and “I found myself in the house of my hated stepfather” (1, 2). He grew up a curious and industrious boy with an aptitude for painting. After primary school he entered the gymnasium, but the lack of financial support soon obliged him to leave. After working as an assistant to a baker, Klaus left for St. Petersburg in 1811 where he became the pupil of a pharmacist. From that day onwards he was independent, with his future in his own hands.

Careful observation and diligence enabled him to become proficient in the work required from a laboratory assistant: analysis, chemistry and pharmacy. In 1815 Klaus passed the examination for pharmacist’s assistant, first class, at the famous Medical Surgical Academy. He then tried to study at the University of Dorpat, but left because he did not want to be dependant upon his relatives. In 1817, having returned to the capital, he passed further examinations at the Academy and became “the youngest qualified pharmacist in Russia” (3). In the same year Klaus became a pharmaceutical chemist in the remote city of Saratov on the lower reaches of the river Volga. Here he worked hard in order to be able to start his own business.

In 1821 he married Ernestina Bate in Dorpat and they moved to Kazan, where he established his own pharmacy. His knowledge, integrity and the wide choice of drugs and herbs he supplied ensured that his pharmacy gained a high reputation. Thus Klaus entered the scientific and cultural circles of the city, and life became easier.

In 1827 Klaus took part in an expedition, led by E. A. Eversman, to study the flora of the steppes around the Volga. The following year Klaus, together with A. Y. Kupfer, organised a research expedition to the Ural, an area known for three centuries as “Russia’s iron spine”, including cities such as Zlatoust, Miass, Ekaterinburg, Neryansk, Nizhni Tagil and Perm. Klaus visited factories, mines, and gold and platinum placer deposits. The report of this expedition, including some excellent illustrations by Klaus, were later published in Paris (4).
Besides his discovery of ruthenium, the sixth platinum group element, Klaus also carried out significant research on rhodium, iridium and osmium. The photograph was taken at the end of the 1850s.

From then on Klaus took a serious interest in the study of the platinum metals.

After the expedition Klaus was at first undecided about his future, but, ignoring all advice, he concluded that:

“I could become very rich, but my striving for scientific education induced me to give up my excellent financial position and take a place as a laboratory assistant at the University in Dorpat” (5).

Thus in 1831, Klaus, then aged thirty-five, sold his drug-store for half the price he thought it was worth and moved his family to Dorpat, determined to study the university course independently, without attending the gymnasium. As twenty years earlier, his persistence and unprecedented devotion to his studies enabled him to achieve his objectives.

In 1835 he was a Candidate of the philosophical sciences, and in 1836 he passed another examination which included questions about “the analysis of platinum ore, with a critical interpretation of the available methods” and “the philosophical faculty did not hesitate to confer upon him the degree of Master” (6).

Professor of Chemistry
The following year Klaus defended his thesis “The Bases of Analytic Phytochemistry” and on the 1st August he took up an appointment in the pharmacy department at the University of Kazan. Once there, however, he was entrusted with the management of the chemical laboratory, lecturing seven or eight times a week and conducting experiments in inorganic chemistry and the chemistry of plants and animals. In December 1839 Klaus was appointed Extraordinary Professor but it was only in 1843 that he became an Ordinary Professor. It is interesting to note that in 1838 the Academy of Sciences awarded K. H. Gebel and Klaus the most prestigious Russian prize for the natural sciences – the Demidov Prize – for their investigations of the flora of the steppes during their 1834 expedition. The award to Klaus was not confirmed (7) and only in 1846 did he receive a Demidov prize, for his ruthenium work.

In the summer of 1840 Klaus travelled to St. Petersburg to obtain equipment. While there he met former colleagues, visited a number of laboratories and the Mint, where two tons of platinum were processed into coins every year.

Ural Placer Deposits
Platinum was recovered from the Ural placer deposits just one year after Emperor Alexander I had issued his edict of 1823, which instructed all mine managers to search for platinum and deliver it to St. Petersburg. A satisfactory process for the large scale refining and agglomeration of platinum, and the technique of manufacturing coins, had been developed in 1826 by the engineer Peter Grigorievitch Sobolevsky (1782–1841). After the platinum had been extracted, however, the insoluble residues, containing the other platinoids, were accumulated without being used.

Emperor Nicholas I took an interest in applications for platinum, visiting Sobolevsky’s laboratory on 12th February 1828. While there he selected patterns for the proposed platinum
coins which were introduced into the currency shortly afterwards. At that time platinum was of much interest in Russia and personal contacts between Klaus and Sobolevsky would have facilitated discussions of the many scientific and technical problems associated with platinum, rhodium, iridium and osmium. Such talks probably influenced the decision of Klaus to involve himself in further work with these metals.

Evidently Klaus, perhaps with the help of Sobolevsky, met Count Egor Frantsevitch Kankrin (1775-1845) the Minister of Finance and obtained support for his research work. It is doubtful (9-11), that Klaus decided from the start "to settle differences" between G. W. Osann and Berzelius concerning the presence or absence of new metals in platinum ore. Osann believed he had discovered three new metals in the ore, but Berzelius did not confirm these results and eventually Osann withdrew his claim. Klaus also identified some very reasonable problems:

"Desiring to study the platinum group metals closely and to prepare their main compounds for the chemical cabinet of the Kazan University, I got two pounds of residue from Sobolevsky and started the work in 1841" (12).

Later, he was to record that:

"my aim was not to discover ... new bodies, but to prepare the compounds. By the way, I accidentally found out the presence of a new body, but I could not separate it at first" (13).

At this time Klaus was forty-six, an age when the creative work curve of many scientists may have reached a plateau, but he was only at the threshold of his creativity. Indeed, on account of his activity, a former student regarded him as quite a young man (14). He devoted himself totally to his labours but suffered greatly from the "endless work in the dense and harmful atmosphere" caused by osmium tetroxide fumes. Despite this he continued his important platiniferous work; and for "two full years I toiled at it from morning till late night, lived only in my laboratory, where I had my dinner and drank tea". The residue he had obtained from Sobolevsky contained "in addition to 10% of platinum, quite a lot of iridium, osmium, some palladium and ... a new body" (15).

At that stage, however, he did not know the characteristics of the latter. Understanding the great importance of his experimental investigations, Klaus journeyed to the capital in July, 1842, where he reported the results of his experiments to Kankrin, and offered to extract the platinum from the residue by the method he had devised. The Minister supported Klaus who was given 8 kg of residue, 100 g of native platinum and the sum of 300 roubles on condition that he would report the results of his work, and return the extracted metals, a year later, see the Scheme. As will be described later, however, it was to be thirteen years before Klaus was able to fulfil these conditions.

Greatly encouraged, Klaus returned home in August, but a major fire in the city affected his laboratory so badly that he was unable to
Another great disappointment occurred when he found much less platinum in the new residue than in the material separated previously. Klaus was to write: “the investigation only remained interesting from a scientific point of view” (15). As before, he worked alone on the new material treating the samples with reagents and systematically studied the resultant sediments, filtrates and residues; he then repeated his investigations and compared the various batches.

Klaus made extensive use of a microscope, probably being the first person to study the platinum metals in this way. He tasted and smelt his preparations, so discovering that the ammines of ruthenium have a more caustic taste than alkalis, while the taste of osmium tetroxide is “acute pepper-like” (8).

Although first identified in 1858, ruthenium tetroxide had been detected earlier by Klaus because of its smell. Klaus set out the results of his experiments very carefully and consequently they can be easily repeated. After establishing the characteristics and distribution of the “new body” and the accompanying platinoids, Klaus found ways of extracting the ruthenium.

His method was based upon the precipitation of double salts of ruthenium and the precipitation of ruthenium from its chloride solution by zinc. Klaus found that on treating chloride salts of ruthenium with hydrogen sulphide a “dense sapphire-blue colour formed. Neither iridium, nor rhodium nor any other metal...” could react in such a way (16).

Klaus eventually extracted 6 grams of metallic ruthenium.

“I named the new body, in honour of my Motherland, ruthenium. I had every right to call it by this name because Mr. Osann relinquished his ruthenium and the word does not yet exist in chemistry” (13).

The first brief announcement, and then fuller reports, about the discovery of ruthenium were sent to the Academy of Sciences at St. Petersburg and to Academician G. I. Gess, who reported them on September 13th and October 25th, 1844. They were later published (17–19).

At the same time Klaus sent samples of ruthenium and a copy of his report to Jöns Jacob Berzelius (1779–1848) in Stockholm. Before
receiving a reply, however, Klaus published his general conclusions about the chemical research he had carried out on the residue of the Ural platinum ore and ruthenium (20, 21). He produced data on the analysis of the residue, described in detail all the characteristics of ruthenium and gave its atomic weight as 104.2. In addition he described: his methods of dissolution, its sulphides, hydroxides, chlorides; some oxides and double salts (20, 21). Their structures and chemical compositions were specified later (22). In platinum from Colombia he found 1.5 per cent ruthenium, but stressed that ruthenium passes from the platinum ore to aqua regia “in such a small amount that it is difficult to find it” (23). He also described some characteristics of the other platinum metals.

**Berzelius’s Final Recognition**

Berzelius quickly examined the material that he had been sent and reported back to Klaus, who was then still an unknown professor, that it was just a dirty salt of iridium; a conclusion that Berzelius published immediately (24). Very upset, but still convinced of his own judgement, Klaus sent additional salts and his latest publication to Berzelius who responded in a letter dated January 24th, 1845, which read:

“Only at the beginning of this month I had the pleasure of receiving your amiable letter dated November 15th, with the enclosure of your article and preparations. My sincere congratulations to you upon the excellent discoveries and their fine processing; .... your name will be indelibly inscribed in the history of chemistry...” (25).

It is stated elsewhere (26) that this was the third letter from Berzelius to Klaus, not the second, but in any case Berzelius only published Klaus’s discovery in 1846, although in that year he informed F. Weller that “its copy [article] was in my hands from November 1844” (27). The scientific progress that resulted from his careful experiments and the soundness of his conclusions made a good impression on his contemporaries and established Klaus as a great authority on the subject. In 1846 the Academy of Sciences awarded him the Demidov Prize for the discovery of ruthenium. He became a corresponding member of the Medical Surgical Academy in 1850 and of the Academy of Sciences of Petersburg in 1861. But Klaus’s priority in discovering ruthenium was doubted not only during his lifetime, but also some 100 years after his death. This matter was considered recently by N. V. Fedorenko (28), co-author of a major text on the platinum metals (29), who proved convincingly that Klaus was indeed the first to discover ruthenium.

In 1852, family reasons obliged Klaus to leave Kazan and return to Dorpat to the Chair of Pharmacy and a laboratory in the University. He was in charge of analytical chemistry. To commemorate the 50th anniversary of the University of Kazan, Klaus published a monograph “Contribution to the Chemistry of Platinum Metals” (30) in which he redefined the chemistry of these metals practically all over again. For a century this was a standard textbook on the subject for scientists, and supported the revival and development of the Russian and Soviet School of Platinum Metals by L. A. Chugaev and I. I. Chernyaev.

In the foreword Klaus wrote:

“I come out with the facts that contradict observations made by the great chemist [Berzelius] and whose memory will remain dear and be revered by me forever. ... The more my experiments contradicted this authority, the greater the care and thoroughness with which I was to check my work, ... the control gave me courage to express everything that turned them into my convictions” (31).

In his monograph Klaus described reliable methods of extracting all six metals in the pure form; together with methods of determining platinoids in the very noble metals (in ruthenium-osmium, iridium; in iridium-ruthenium, platinum, palladium, rhodium; in rhodium-ruthenium, iridium, platinum and others); characteristic reactions for every platinum metal with 15 reagents are given; the mutual influence of platinoids on their specific reactions, for example 15 pairs (ruthenium + iridium, ruthenium + osmium, rhodium + iridium, ruthenium + platinum and others); schemes of quantitative analysis of platinum materials; and comparative characteristics of the most complicated pair, namely iridium and rhodium. For the first time Klaus stressed that reactions with salts of
platinum metals proceed slowly and need a lot of time or heating.

Finally, in the chapter “About Platinum Bases” Klaus showed the change in molecular characteristics after their co-ordination by a metal; for the first time he considered ammonium compounds “as compounds of the passive [co-ordinated] ammonium with metal oxides, where the ability for saturation depends on the metallic oxide” (32).

Thus, Klaus was not only an outstanding experimenter working in breadth, but also a perspicacious scientist, simultaneously investigating topics in depth. These concepts were difficult for his contemporaries to understand and were only developed later in Alfred Werner’s co-ordination theory. “Werner’s views represent a new modification ... of the theory of combinations by Klaus” (N. S. Kurnakov, 1893); Klaus’s concepts “appeared again nearly 40 years later in Werner’s co-ordination theory” (G. Kauffman, 1976) (33).

But this is not all; in a nine-page chapter on cyanic compounds, Klaus comes to a fundamental “unexpected” conclusion. “Platinum metals according to their likeness can be grouped in pairs: platinum and palladium, iridium and rhodium, osmium and ruthenium. Every main metal from the platinum group: platinum, iridium and osmium, having nearly the same atomic weight, ... have next to them another metal of approximately half of their atomic weight, which is very closely connected by similar properties and morphologies ... This resemblance is ... so definite, that it cannot be doubted at all” (34).

Klaus’s observations about the changing characteristics of the triads, Ru-Rh-Pd, Os-Ir-Pt, both across and down, led Mendeleev to conclude that the platinum metals belonged in one group (VIII) of his Periodic Table. Mendeleev formulated his Periodic Law in 1871 in the “Bases of Chemistry” and in a chapter on “Platinum and its associates” a section was devoted to “Ruthenium and osmium anhydride” (35).

It is interesting to note that at much the same time as Klaus was working on problems concerning the platinum metals, he was also involved in extensive work with the Academy of Sciences on Russian flora. His monograph of scientific descriptions of thousands of plants, including eight species that he discovered, was first published in German and later in Russian (36).

From the mid-1850s Klaus began to work on a “complete monograph on platinum metals” with sections on their history, chemistry, analysis and metallurgy. The Deville and Debray method of fusing platinum was started between 1857 and 1859 and appeared to offer an opportunity of manufacturing platinum articles more readily than the established “wet” methods of consolidation. Klaus was well informed about this and also knew about the smelting work carried out by I. I. Varvinsky (1797–1838) who, as early as 1836, had melted platinum using an oxy-hydrogen flame (37), although his method did not attract any attention at the time. The possibilities of fusing platinum were studied by B. Yakobi who visited Deville and Debray in 1859 on the instruction of the Russian government. In Paris, Yakobi conducted the fusion
of 30 kg of platinum and obtained an iridium ingot weighing 1.8 kg (38). Klaus, an old friend of Yakobi, was aware of the results of his experiments. However, Klaus was more interested in the chemical characteristics of fusion, that is, the behaviour of the platinum metals and their admixtures during melting.

In order to become better acquainted with the work being carried out on the platinum metals in the rest of Europe, to study the scientific literature and to investigate the chemical aspects of fusion, Klaus arranged a trip to western Europe, leaving Russia for Berlin in the middle of May, 1863. He was treated as a celebrity – receiving well-deserved respect and honours. In Berlin he was elected a corresponding member of the Prussian Academy of Sciences, and met with Gustav and Heinrich Rose, Gustav Magnus and Poggendorf. In Hanau he made the acquaintance of W. C. Heraeus, who, like him, had been a pharmacist before starting his own business, and who was now the head of a small platinum workshop. Klaus took part in experimental fusions with Heraeus, and discussed with him the benefits and problems associated with fusion in the lime furnace, Klaus expressing his doubts about the universality of the method (39, 40).

Klaus then went to Switzerland and later to Paris, visiting the works of Henri Saint-Claire Deville, Chapuis and H. K. Desmoutis and F. A. Quennessen. He associated with C. A. Wurz, M. Berthelo, E. Fremi and other scientists, and studied the scientific literature. While there Klaus again took part in fusion processes, discussing the results and receiving presents of platinum artifacts and preparations (39, 40).

**Klaus Visits Hatton Garden**

Late in the Autumn of 1863 Klaus left for London to visit Johnson Matthey. He was particularly interested in this firm because he knew that it had recently purchased a large quantity of Russian platinum and platinum residues. Although “no record of such a visit has so far been found” by Johnson Matthey (11), Klaus reported that George Matthey received him “with the same obligingness as the French manufacturers showed me and allowed me into his laboratory”. Thus Klaus became more knowledgeable about fusion furnaces, laboratories and the methods used to analyse the platinum metals. During discussions with George Matthey, Klaus expressed his doubts about the suitability of the fusion method for processing virgin platinum or platinum residues because they include much rhodium and iridium. Klaus was later to write “Mr. Matthey, a devotee of the method of fusion, also had to recognise that this method could not be used in the case of platinum ore”, while on parting “Mr. Matthey very amiably made me a present of several samples of platinum preparations” (39, 40).

**Klaus’s Death**

At the beginning of January 1864, Klaus travelled back to Dorpat and returned to work. At the end of February he gave a lecture to
was made by sledge, he caught a chill and was ill when he reached home on March 10th. To everybody’s surprise Klaus died of pneumonia on March 12th. He was buried in Dorpat but his tomb was not preserved.

The monograph that Klaus had been preparing was never completed, but following his death the parts of it that could be found were published (40) by one of his pupils, A. M. Butlerov, who had later succeeded him at Kazan.

Without Klaus the study of ruthenium in Russia practically ceased and was not resumed until the 1930s, when it was revived by Professor Orest Evgenyevitch Zvyagintsev (1894-1967) and further advanced by his pupils, Nikolay Mikhailovitch Sinitsyn (1931-1992) and the present author. Indeed, between the early 1930s and 1990s, there were around 400 papers published by them in Russia on ruthenium and other platinum metals, including 11 monographs.

References

1. N. N. Uschakova, “Karl Karlovitch Klaus”, Nauka, Moscow, 1972, p. 8
2. Archives AN USSR, Russian Academy Sci., (Leninskii str., 14, 117 071 Moscow), arch. 66, list 2, file 59, p. 29, (Ref. 1, 8)
6. Central State Historical Archives of Estonian SSR, (C.G.I.A. ESSR), arch. 402, University of Dorpat, list 2, file 785, p. 25 (Ref. 1, p. 29)
9. B. N. Meuschutkin, Izv. Inst. po Isucheniju Platini, 1928, 6, p. 6
11. D. McDonald, Platinum Metals Rev., 1964, 8, (2), 67
14. A. M. Butlerov, Izbr. trudi, Moscow, 1961, 3, 96
20. K. Klaus, “Chimicheskoe issledovanie ostatkov uralkoii platinovoj rudi i metalla ruthenii”, Uch. zan. Kazan University, (Collection of Works), 1844, (3)
21. K. Klaus, “Chimicheskoe issledovanie ostatkov uralkoii platinovoj rudi i metalla ruthenii”, in “Kazan”, 1845
24. Jahres-berrytuber die Fortschritte der Chemie und Mineralogie von Berzelius, 1845, Jg., 24, p. 28, (Ref. 2, p. 49)
30. K. K. Klaus, “Flori mestnii privoljsich stran”, St. Petersburg, 1883,62
38. B. S. Yakobi, Gorn. Zh., 1861, pp. 32, 237, 400
40. J. Ministerstva Narodnogo Prosvescheiy, 1864, Ch. 12, (4-6), pp. 612-621, (Ref. 1, p. 91)
41. K. Klaus, “Fragment einer monographie des Platins und der Platinmetalle, 1865-1883”, St. Petersburgh, 1883, p. 62