

William Hyde Wollaston

The platinum group metals and other discoveries

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Resumen

William Hyde Wollaston (1766-1828), inicialmente educado como médico, fue uno de los más consumados químicos de su tiempo. Nos dejó importantes contribuciones en un amplio rango de actividades: patología, fisiología, química, electroquímica, óptica, mineralogía, cristalografía, electricidad, mecánica y botánica. Wollaston desarrolló el primer método viable para aislar el platino y hacerlo dúctil, descubrió el paladio y el rodio, desarrolló una regla de cálculo para calcular equivalentes. Introdujo un prisma que lleva su nombre, un goniómetro reflexivo para medir los ángulos de un cristal, demostró que el agente de la electricidad de fricción es el mismo que el de la pila, introdujo un refractómetro de lectura directa y desarrolló lentes para usos ópticos. Además, estudió los cálculos biliares e identificó la cistina.

Abstract

William Hyde Wollaston (1766-1828), initially educated as a physician, was one of the most accomplished chemists of his time. He left us with significant contributions in a wide range of activities: pathology, physiology, chemistry, electrochemistry, optics, mineralogy, crystallography, astronomy, electricity, mechanics, and botany. He developed the first viable method for isolating platinum and making it malleable, he discovered palladium and rhodium, developed a slide rule for calculating the chemical equivalents, introduced a prism that carries his name, a reflective goniometer for the measurement of crystal angles, demonstrated that the agent of frictional electricity was the same as that in a pile, introduced a direct reading refractometer, and developed glasses for different optical use. He studied urinary calculi and identified cystine.

Life and career (Cragg 1966; Gilbert, 1952; Halsted, 1849; King, 1954; Wayling, 1927)

William Hyde Wollaston (Figures 1 and 3) was born on August 6, 1766 in East Dereham Norfolk, the third son of

Reverend Francis Wollaston (rector of East Dereham) and Althea Hyde.

In 1762, his father with his wife and newborn son, Francis John, moved from London to become rector of the parish in East Dereham, a village 16 miles from Norwich. The Wollastons were a distinguished, well to do and well known family in ecclesiastical, medical, and scientific circles. Great grandfather William, a distinguished clergyman, had published a book *The Religion of Nature Delineated* (Wollaston, 1722) in 1722 which went through many editions, and his reputation was one reason why the younger William preferred to use William Hyde in all official literature. Francis's younger brother, George, became a clergyman and fellow of the Royal Society, while another brother, Charlton, practiced medicine at Bury St. Edmunds and in 1764 was appointed Physician-in-Ordinary of Queen Charlotte (1744-1818; consort of George III). From East Dereham the family moved to Chislehurst, Kent, where in 1777 Francis served as precentor of St. David's and in 1779 rector of the united parishes of St Vedast, Foster Lane, and St. Michael-le-Querne, Aldersgate, Kent, until his death in 1815. Despite the load of domestic and parochial duties, Francis Wollaston wrote on theological topics, became Fellow of the Royal Society, practiced as an amateur astronomer, compiled a catalogue of circumpolar stars (Wollaston, 1800) and with a barometer and thermometer collected data for obtaining mean monthly weather readings throughout the year based on his own observations (King, 1954).

At the age of six William Hyde was sent to a private school at Lewisham, London, and two years afterwards to Charterhouse School (then located in London), a school situated a few minutes away from his grand parents home, for a further four years of education. On July 6, 1782 he was admitted as pensioner of Gonville & Caius College, Cambridge, to study medicine. He was appointed a senior fellow of the College in 1787, a fellowship, which he retained until his death. He received his Medicine Bachelor degree in 1787 and Medicine Doctor in 1793, having waited the stipulated five years. He was also Tancred student, held the offices of Greek and Hebrew lecturer, and was repeatedly appointed to make the Thurston speech. At Cambridge, Wollaston attended lectures in astronomy and mathematics. Among his classmates in the course of Astronomy were John Brinkley

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(1766-1835), who would become Astronomer Royal for Ireland, and John Pond (1767-1836), who would be appointed Astronomer Royal at Greenwich, in succession to Neville Maskelyne (1732-1811) (King, 1954). George Peacock (1791-1858) says that Wollaston “was a good geometer, a good optician, and thorough master of mechanical principles, as far as his limited knowledge of analysis would enable him to apply them” (Peacock, 1855).

In 1787 Wollaston moved to London to forward his medical studies by attending lectures and walking the hospitals, and eventually, in 1789, he took up practice for only a few months at Huntington. From there he moved to Bury St. Edmunds where his uncle, Dr. Charlton Wollaston, had practiced. Here he met the Rev. Henry Halsted (1771-1852), fellow of Christ’s College, Cambridge, who became a life-long friend. Years after Wollaston’s death, Halsted would write his biography and give personal information about their friendship (Halsted, 1849). On May 9, 1793, Wollaston was elected Fellow of the Royal Society. His certificate describes him as “William Hyde Wollaston, of Huntington, doctor in physics, of the University of Cambridge”, and has 13 names attached to it, among which appears Henry Cavendish (1731-1810), William Herschel (1738-1822), and two Wollastons, his father and his uncle. On March 30, 1795, Wollaston became Fellow of the Royal College of Physicians, of which he became censor in 1798 and member on February 13, 1824, after the death of James Harvey (King, 1954).

In 1797, after several lucrative years as a physician in Huntington and Bury St. Edmunds, he moved to London where he set up practice at 18 Cecil Street, Strand. Here he wrote his first paper (Wollaston, 1798) for the Royal Society, dealing with gouty and urinary concretions; an investigation of the chemical composition of calculi, which resulted in the discovery by Wollaston, of cystic oxide, now called cystine. About the same time he became a candidate for the post of physician to St. George’s Hospital but was defeated by the election of his principal opponent, Dr. Pemberton. In 1800 Wollaston decided to retire from medical practice because he was over-sensitive about the conditions of his patients, constant anxiety over their welfare made light work a heavy burden, and was deeply affected by trivial illnesses. In 1799 his brother George, who had inherited the estate of their mother’s heirless brother General West Hyde, gave him £8000 in Bank of England stock and in 1801 his uncle Frederick, the Rector at Bury St. Edmunds, died and left him enough money, so that Wollaston, now without financial worries, was at liberty to follow his scientific inclinations and undertake private chemical research. In 1801 he purchased a house near Fitzroy Square, and at the back set up a laboratory. To equip and maintain a private laboratory and give private classes was a common activity among European

scientists in those days.

In 1800 Wollaston formed a secret partnership with Smithson Tennant (1761-1815), another non-practicing physician of independent means with who he had become friend at Cambridge, to share expenses and income from chemical manufacturing business. One of the first enterprises they addressed to was the possibility of manufacturing malleable

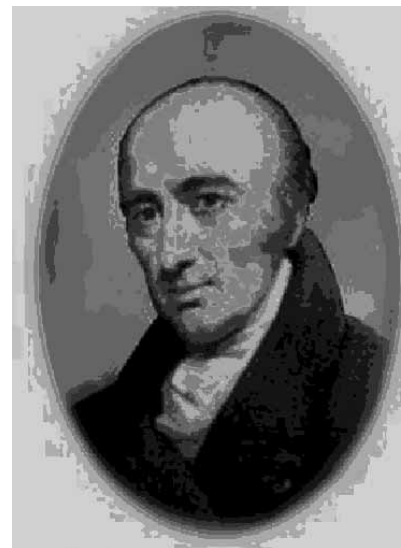


Figure 1. William Hyde Wollaston (1766-1828).

platinum. They were aware that if they succeeded, malleable platinum could replace gold in a number of applications where an inert, noble metal was required. Many scientists had recognized the commercial market for malleable platinum before, but none had succeeded in developing a satisfactory commercial procedure. Within five years Wollaston had discovered a process for producing pure platinum and for rendering it malleable (Wollaston, 1809a; 1829). Briefly the process took place by dissolving native platinum in aqua regia, precipitating ammonium chloroplatinate with ammonium chloride, decomposing it by heat, washing the finely divided residue of platinum, compressing the moist powder, beating while hot and hammering to an ingot which could be beaten into foil or drawn into wire. This method was the first application of powder metallurgy. Wollaston showed that very fine wires of platinum could be drawn inside a silver sheath and the silver afterwards dissolved off in dilute nitric acid. Using this method Wollaston was able to produce without difficulty wires of a diameter 0.00005 inches (Wollaston, 1813b). These wires, called Wollaston’s wires, are still made commercially by the same method, and used as marks in optical instruments.

Platinum became a valuable commercial metal in 1805 when Wollaston began marketing it through William Cary (1759-1825), an instrument maker in the Strand, London. The primary use of malleable platinum was in the making of vessels for the distillation of sulfuric acid. It was thus of great commercial value and earned Wollaston quite a sizable fortune from various manufacturers (Cragg, 1966). According to King (King, 1954) in addition to this venture, royalties on his other processes and inventions added considerably to

Wollaston's income so that at his death he was estimated to be worth between £200,000 and £300,000. Wollaston kept his method of rendering platinum malleable secret until a few weeks before his death he revealed it to the Royal Society (see below).

The work on platinum led to the discovery of palladium (Wollaston, 1805a) and rhodium (Wollaston, 1804b). It is interesting to note also that when Michael Faraday (1791-1867) undertook a series of experiments to improve flint glass manufacture in England, he tried platinum trays and stirring rods. Faraday wrote: "Platina also was ultimately found to answer perfectly the purpose of retaining the glass...neither the glass nor any of the substances entering into its composition...had the slightest action upon it...The instrument used for stirring the glass...consisted of a piece of plate platina...perforated with various irregular holes that, when drawn through the glass like a rake, it may actually mix the parts (Faraday, 1830)."

Wollaston's discoveries were numerous and from 1800 on he made many contributions to science. He was one of the most accomplished chemists of his time, but he also made important contributions in the fields of pathology, physiology, chemistry, electrochemistry, optics, mineralogy, crystallography, astronomy, electricity, mechanics, and botany (Cragg, 1966). Altogether, he wrote 56 papers on a wide range of subjects, 40 of which were read to the Royal Society and published in its *Transactions*. According to King (King, 1954) Wollaston's knowledge of matters scientific was so ample and generally infallible that his friends familiarly referred to him as "the Pope".

In addition to chemistry and metallurgy, he committed a great deal of his time to optical phenomena and instrumentation. In 1809 he invented the reflective goniometer for the measurement of crystal angles and used it to demonstrate that the rhombohedral angles of calcite, dolomite, and iron spar are different (Cragg, 1966; Wollaston, 1809b). In 1820 he introduced his now well-known prism (Wollaston, 1820), which significantly improved the device built by the Abbé Alexis Marie Rochon (1741-1817) and used in reflecting telescopes. When Rochon's prism was slid along the optical axis of the object glass, a single distant object appeared double and under different visual angles. Wollaston explained how to cut and form two quartz wedges so as to build a prism capable of giving double the angular separation of the Rochon prism.

In 1814 Wollaston published a paper on theoretical chemistry (Wollaston, 1814) on which he proposed replacing Dalton's atomic weights by chemical equivalents, a step which subsequently gave rise to much confusion by reason of the unfortunate choice of the term equivalent (Hinde, 1966).

By 1804 he had delivered a Bakerian Lecture, had been awarded the Copley Medal of the Royal Society for papers contributed to the *Philosophical Transactions*, and had been elected Junior Secretary of the Royal Society, a post he held for twelve years. In the latter position he was at the center of things dealing with natural philosophy. Wollaston served several times as vice-president of the Royal Society and in 1820, after the death of Joseph Banks (1778-1820), its President; he declined a proposal to replace him. He acted as interim President until Humphry Davy (1778-1819) was elected for the post. In 1823 he had the distinction of being elected one of the eight foreign associates members of the Académie des Sciences. In 1812 he was elected Fellow of the Geological Society and in 1828, member of the Astronomical Society (Wayling, 1927).

In his second Bakerian lecture, entitled "On the Elementary Particles of Certain Crystals" (Wollaston, 1813a), read on November 26, 1812, Wollaston showed that many crystalline forms could be built up by assuming that the unit molecules are spherical, an idea that afterwards he found had already been suggested by Robert Hooke (1635-1703). He also discussed his findings about the change of solubility of crystals of different size with temperature: a change in atmospheric temperature resulted in an increase in the size of larger particles and a decrease in the smaller ones (today we know that because of surface forces fine particles can have an appreciable larger solubility than large crystals of the same substance).

By 1814 Wollaston was famous enough to be called repeatedly to serve the public interest. During the next decade he served on twelve different committees appointed to investigate the cause of explosions in gas works, ascertain the utility of Charles Babbage's (1791-1871) machine for calculating and printing mathematical tables, for determining the length of a pendulum beating seconds, to inquire into a mode of preventing forgery of banknotes, etc., etc. (Wayling, 1927). In 1814 he appeared in front of a committee of the House of Commons and recommended the replacement of the various gallons then in use by the imperial gallon (adopted in the Weights and Measures Act of 1824). Between 1818-1828 he served as commissioner of the Royal Society on the Board of Longitude, and in 1819 as member of the Royal Commission on Weights and Measures that rejected the adoption of the decimal system of weights and measures.

During 1827 and 1828 Wollaston suffered some physiological problems that resulted in numbness in the left arm and lack of response of the left pupil to changes in light intensity, which his physician diagnosed were caused by a brain tumor. Wollaston died on December 22, 1828 and was buried at the parish church of Chislehurst, Kent, the church in which his father preached for many years.

Scientific contribution

1. Platinum and platinum group metals

(a) *Platinum*

Platinum was isolated and used in malleable form well before Wollaston became interested in it. The methods used for separating it from the ore and making it malleable were unreliable, inconsistent, and led sometimes to mechanical failure of the fabricated ware. There was no real fundamental knowledge of the composition of the native mineral or of the nature and properties of the products derived from it (McDonald, 1966). When Wollaston and Tennant decided to investigate the problem they faced a serious shortage of raw material. All the known deposits of platinum ore were located in South America, there was war between France and England, and, in addition, the King of Spain had prohibited its export because of fears that it could be used to adulterate gold. The only available “commercial” sources were the small amounts smuggled from the Spanish territories to Jamaica, which eventually would find their way to London. Tennant and Wollaston’s efforts allowed them to purchase 5959 troy oz (185 kg) for £795, in 1800 and an additional 800 oz (24.9 kg) in February 1801 from Richard Knight (1768-1844), who had earlier published a paper on the purification of platina ore (Knight, 1800). These purchases secured the whole British supply for the chemical entrepreneurs while Wollaston applied his considerable chemical talents toward a purification process.

In a carefully planned series of chemical experiments done in 1800, Wollaston developed a viable process by which the crude ore was selectively dissolved into aqua regia, precipitated by sal ammoniac and heated to give residual platinum powder. Wollaston’s experiments, as recorded in his notebook, established the necessary weights of all reagents and the precise operating conditions. He used his procedure to treat about 50,000 troy oz (1,550 kg) of platinum ore, mostly in 32 oz batches, to produce pure platinum in ingot form, and contracted the services of William Carey to sell the bulk of the produce. Although Wollaston had initially intended to market only small platinum implements such as crucibles and evaporating pans, large markets opened up in the gunnery business (platinum was used for touch-holes, the metallic orifices in flintlock firearms through which the gunpowder was ignited) and sulfuric acid manufacture. Sales of platinum up to the 1820s amounted to about £30,000.

As mentioned above, Wollaston kept the details of the chemical purification and metallurgical compaction processes secret for a long time, but published them shortly before his death in 1828 (Wollaston, 1829). Either because potential competitors believed that his secret process contained details

not easy to rediscover, or crude ore was unavailable, he had no British competitors. He wrote: “As from long experience, I am probably better acquainted with the treatment of Platina, so as to render it perfectly malleable, than any other member of this Society... The usual means of giving chemical purity to this metal... are known to every chemist; but I doubt whether sufficient care is usually taken to avoid dissolving the Iridium contained in the ore, by due dilution of the solvent... The yellow precipitate is well washed... well pressed... next heated with the utmost precaution... with so low a heat as just to expel the whole of the sal ammoniac and to occasion the particles of platina to cohere as little as possible; for on this depends the ultimate ductibility of the product” (Wollaston, 1829).

According to McDonald (McDonald, 1966) the essential points of Wollaston’s process were that the aqua regia used for dissolving the mineral should be diluted (about 50:50) to avoid dissolving the iridium. The yellow precipitate produced by sal ammoniac was washed and pressed well, before being gently heated at low temperature to produce platinum sponge. Wollaston claimed that it was critical that the temperature do not exceed this level and, in any grinding required the metal should not be burnished. The sponge was then hand rubbed into a fine and uniform powder, which was then washed and elutriated with water. After decantation, the supernatant water was eliminated and the residual mud transferred to a brass mould, which was closed with a steel stopper wrapped in blotting paper and wool to gently press out the excess water, followed by hard pressing. This produced a cake of metal, which was then exposed to the highest temperature attainable and then forged by hand in an anvil. An ingot of about 22 oz of malleable platinum resulted and this could be hammered into sheet or drawn into wire (McDonald, 1966).

As we can see, this method had two key innovations: the use of aqua regia with the most effective molar ratio (4:1) of hydrochloric to nitric acids and in amount sufficient to dissolve only about half of the crude ore. These improvements gave platinum powder in the subsequent precipitation step that was consistently over 98 per cent pure.

By 1810 the process invented by Wollaston became established for the production of large batches of platinum: First, gold was removed by dissolving the raw material in aqua regia, and then the excess acid was boiled off. The dissolved platinum was precipitated as ammonium hexachloroplatinate, and the gold chloride separated by washing. The remaining solid was calcined yielding platinum sponge. Metals such as iron, copper, and manganese, were removed by treating the metal grains with strong nitric and hydrochloric acids alternatively until the base impurities were removed. The platinum was then re-dissolved in aqua

regia, precipitated with ammonium chloride, and reduced by gradually raising the temperature to red heat. To prevent precipitation of the other metals of the platinum group, the solution in aqua regia was freed as much as possible from excess acid, and nitric acid was added before precipitation with ammonium chloride. The platinum black, or powder obtained in this manner was pressed and beaten into sheets.

Wollaston used his procedure to manufacture crucibles and other laboratory ware by means of special moulds into which the powder was rammed. The moulds were then heated in an air furnace, subsequently in a very hot blast, and finished off on the anvil. He manufactured very large boilers of platinum capable of holding 300 pounds of sulfuric acid and showed that extremely fine wires of platinum would be drawn inside a silver sheath, which was afterwards dissolved with dilute nitric acid (Wollaston, 1813b). The boilers were usually truncated cones, each narrowing slightly to a bottom that was convex externally, and were fitted with a rim apparently designed to sit in a water seal. Their weight varied between 322 to 427 ounces and the price did not exceed £400. A 45-gallon boiler would yield over 5 cwt of sulfuric acid per boiling.

Approximately three quarters of Wollaston's total output of malleable platinum was commercially marketed for him by William Cary.

(b) *Iridium and osmium* (Wisniak, 2006)

During their study of the properties of platinum many scientists had noted that the precipitates of platinum chloride with ammonium or potassium chloride presented different colorations but these were not always yellow as expected. Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829) investigated the residue left by the action of aqua regia on native platinum ore and found that it precipitated a red platinum chloride. From these results they concluded that it contained a new metal: "Tout an-nonçait que le poudre noire contenait un metal nouveau (Everything points out that the black powder contains a new metal) (Vauquelin and Fourcroy, 1804, 1806). This statement was also reinforced by the findings of Hyppolyte Victor Collet-Descotils (1773-1815) who stated that the color of some salts of crude platinum were due to a new metal, which he did not isolate (iridium). In his research Collet-Descotils also examined the metal found with native platinum, which has "une grande résistance à l'action des acides" (has a great resistance to the action of acids) (now called os-miridium) (Collet-Descotils, 1803). Vauquelin and Fourcroy (Vauquelin and Fourcroy, 1804, 1806), also confounded iridium and osmium, ascribing both to a single metal they called *ptene*.

In 1804 Tennant decided, "to experiment on the black

powder, which remained after the solution of platina and I observed that it did not, as was generally believed, consist of plumbago, but contained some unknown metallic ingredients" (Tennant, 1804). He was aware that Collet-Descotils (Collet-Descotils, 1803) and Vauquelin and Fourcroy (Vauquelin and Fourcroy 1804) suspected the presence of only one new metal in the black powder, but Tennant believed "that it contains also another metal, different from any hitherto known." He analyzed the material using a method similar to that employed by Vauquelin, namely, "the alternate action of caustic alkali and of an acid": the powder was mixed in a crucible of silver with a large of pure dry sodium hydroxide, kept in a red heat for same time, and then washed with water. The alkali solution had a deep orange or brownish-yellow color. The remaining powder was now digested with hydrogen chloride giving a dark blue solution, which then became of a dusky olive green, and later, on continued heating, attained a deep red color. According to Tennant the alkaline solution contained the "oxide of a volatile metal, not yet noticed and also a small proportion of the second metal." The volatile oxide could be separated by acidification and distillation. It was a colorless body, condensing first to an oily liquid and then solidifying into a semi-transparent mass. In all stages it had a strong and very characteristic smell. It was this that led Tennant to name the metal *osmium*, from a Greek word meaning smell. With regards to the other metal, Tennant's work confirmed and extended the observations of Vauquelin and Fourcroy (Vauquelin and Fourcroy, 1804, 1806) on the subject and led him to name the second element *iridium* "from the striking variety of colors which it gives while dissolving in marine acid." For this discovery the Royal Society awarded Tennant the Copley Medal, awarded annually to the person judged to have undertaken and published the most important investigation upon any subject of natural history in the preceding year.

c) *Palladium*

Wollaston studied the solution of native platinum in aqua regia using a similar procedure as that of Tennant, but directed his attention to the liquid phase remaining after the addition of sal ammoniac, being curious about the nature of any non-platinum components. He suspected that something new was present in it, remaining in the solution after the precipitation of platinum by sal ammoniac, which was neither platinum nor Tennant's iridium. He first neutralized the solution with soda and then introduced in it bars of iron to recover the dissolved platinum, as well as other substances which he believed were present. The new precipitate was a fine, very black powder. In 1802 he discovered that adding mercury prussiate (mercuric cyanide) to the waste solvent

gave a precipitate that, on heating, yielded a metal quite different from platinum, which he called *palladium* after the asteroid Pallas that had just been discovered by Heinrich Wilhelm Olbers (1758-1840) (Wollaston, 1804b, 1805a). By pooling and treating large amounts of waste solvents, Wollaston prepared palladium in troy oz quantities.

This discovery presented Wollaston with a difficult problem, he wanted to publish his results but at the same time he did not want to hurt his platinum business. He solved the problem on a strange manner, which had some unpleasant consequences. He decided to offer samples of palladium for sale anonymously in 1803, through the Soho mineralogical shop of Jacob Forster and so, near the end of April of that year, several members of London's scientific community received a small printed notice in the mail advertising the properties of a new noble metal dubbed *Palladium* or *New Silver*. The small leaflet listed several distinguishing properties of the new metal, and announced that it could be purchased at the Forster shop, in samples of five shillings, half a guinea, and one guinea. The notice did not indicate the source of the new metal, or the procedure employed for its isolation and purification, or the identity of its discoverer. Nicholson, the editor of the *Journal of Natural Philosophy, Chemistry and the Arts*, received a copy and printed the notice in his journal (Kronberg, 1981; Nicholson, 1803; Usselman, 1978).

Richard Chenevix (1774-1830), a chemist, read the palladium notice on April 19, 1803 and was piqued by its contents, believing that the notice was a bad taste prank. He put himself to study the metal, and on May 12, after 13 days of research, read a 31-page paper to the Royal Society (Chevenix, 1803) where he declared that the unusual announcement of the discovery of the new metal hinted of fraud, and although the metal had all the advertised properties, he believed it was actually an alloy of platinum and mercury. Chenevix even suggested that the palladium came from someone "without education, ... [whose] chemical language and phrases sound like Alchemy", maybe even "a hair dresser at Islington" (Chevenix, 1803). He tried by many different methods to synthesize the new metal from platinum and mercury, without success, but wrote: "It certainly is one of the most extraordinary facts respecting alloys that two metals, by their own union with each other, should so lose the characteristic properties of each individually, that neither of them can be immediately detected by the usual methods. Nothing but an affinity of the most powerful order could produce such effects... From the repeated failures which I have experienced in these operations, I am much inclined to think that the author of palladium has some method of forming it, less subject to the error of any I have mentioned. No doubt that perseverance would

put us in possession of hi secret" (Usselman, 1978).

Wollaston, having tried in vain to prevent the reading of the paper, then put a anonymous notice in *Nicholson's Journal of Natural Philosophy Chemistry and Arts* (Nicholson, 1804) offering £20, to anyone who could succeed in making only 20 grains of real palladium, before three competent "gentlemen chymists", the Editor being one of them, the unknown correspondent stating that his reason for not saying where the metal was found was that he might make some advantage of it, as he had a right to do. No one came forward to claim the prize.

The President of the Royal Society, Joseph Banks, had no choice but to involve himself in the discussion. Near the end of 1803 the Royal Society began the process of choosing candidates for reception of the Society's annual awards. The top candidate for the Copley Medal, was Richard Chenevix, chiefly for his paper on the compound nature of palladium (Wollaston had received the Copley Medal himself the previous year). Hoping to save the Royal Society of any embarrassment, which might result from an award based largely on a publication, which was substantially in error, Wollaston confided to Banks that he was the discoverer of palladium, and asked him to guard the secret. Since Banks was in no position to know whether Chenevix or Wollaston was correct, hence he disregarded Wollaston's information and Chenevix was awarded the medal (Usselman, 1978).

Eventually Wollaston revealed his identity as the discoverer in a communication to the Royal Society (Wollaston, 1805ab).

Wollaston described his procedure for making malleable palladium in the same paper he did it for platinum: "To obtain malleable Palladium, the residuum obtained from burning the prussiate of that metal is to be combined with sculpture, and each cake of the sculptured, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little niter. The sculptured is roasted... until it becomes spongy on the surface. The ingot is then cooled... tapped with a light hammer to beat down the spongy excrescences on its surface" (Wollaston, 1829).

The preparation of palladium was described as follows: "To a solution of crude platina in aqua regia, whether rendered neutral by evaporation of the redundant acid, or saturated by addition of potash, of soda, or ammonia, etc., it is merely necessary to add a solution of prussiate of mercury for the precipitation of palladium. The precipitate obtained consists wholly of prussiate of palladium, and when heated will be found to yield that metal in a pure state. Mercuric prussiate is so selective that it can be used as a test to detect the presence of palladium in any of its solutions. When the palladium has been dissolved in nitrous acid and precipitated from a neutral solution by mercuric prussiate, the precipitate

this formed has the property of detonating when heated to about 5,000°F” (Wollaston, 1804b).

(d) *Rhodium*

Earlier, in the summer of 1804 while the palladium controversy was going on, Wollaston isolated another new metal from the waste acids. He named this new element rhodium and published details of its discovery immediately after its isolation; apparently he had no desire to initiate a second dispute. He dissolved a portion of crude platinum in aqua regia, and neutralized the excess acid with caustic soda. He then added sal ammoniac to precipitate the platinum as ammonium chloroplatinate, and mercuric cyanide to precipitate the palladium and palladious cyanide. After filtering the precipitate, he decomposed the excess mercuric cyanide in the filtrate by adding hydrogen chloride and evaporating to dryness. When he washed the residue with alcohol, everything dissolved except a beautiful dark red powder, which proved to be a double chloride of sodium and the new metal, $\text{Na}_2\text{RhCl}_6 \cdot 18\text{H}_2\text{O}$, which because of the rose color of its salts, Wollaston named rhodium (Wollaston, 1805b). He found that the sodium rhodium chloride could be easily reduced by heating it in a current of hydrogen, and that after the sodium chloride had been washed out, the rhodium remained as a metallic powder. He also obtained a rhodium button, which was not malleable as were both platinum and palladium.

Wollaston’s discovery of rhodium completed the identification of all the platinum group metals.

Palladium and rhodium remained as curiosities during most of the nineteenth and Wollaston was unable to sell his store of the metals, although he attempted to discover applications for them. Production increased very slowly; the breakthrough came with the discovery of the extraordinary catalytic properties of the platinum metal group. Today these metals stand at the heart of the petrochemical industry and are the basis of all the means for controlling the emission of obnoxious gases of motor vehicles.

Berzelius received some samples of the new metals from Wollaston and them to prepare different compounds of rhodium, the various oxides, nitrate, sulfate, and persulfate, and using the laws of chemical proportions determined their composition. He also found that there was only one oxide of palladium and determined its elemental composition. In his publication he listed the symbols and specific weight of the elements known then. Table 1 contains these interesting values (Berzelius, 1814ab).

2. *Chemical theory*

Wollaston wrote two papers on chemical subjects, which are of significant theoretical interest: *On Super-Acid and Sub-Acid Salts* (Wollaston, 1808), and *A Synoptic Scale of Chemical*

Table 1.

| Element | Symbol | Weight in form of gas | Atomic weight |
|-----------|--------|-----------------------|---------------|
| Oxygen | O | 100.00 | |
| Osmium | Os | | 198.94 |
| Iridium | I | | 196.7 |
| Rhodium | Rh | 1,490.31 | 104.31 |
| Platinum | Pt | 1,206.7 | 197.10 |
| Palladium | Pa | 1,407.5 | 106.22 |

Equivalents (Wollaston, 1814). The first one is a description of his experiments on carbonates, sulfates, and particularly oxalates, which proved that the composition of these substances was in harmony with the law of multiple proportions. For example, he measured the volumes of carbonic acid (CO_2) liberated by the action of acid (or heat) on known weights of carbonate and bicarbonate (sub-carbonate) of potassium (or sodium) and found that they were in the ratio of one to two respectively. From these results he concluded that potash combined with a certain weight of carbonic acid to form the acid carbonate and with twice this weight to form the neutral carbonate. He found the same results when dealing with potassium sulfate and potassium bisulfate. His analysis of potassium oxalates showed that a fixed weight of potassium would combine with three different weights of oxalic acid to form distinct salts. The weights of oxalic acid were in the proportions of 1:2:4, and the absence of a compound with three portions of acid seemed anomalous, but he explained: “To account for this want of disposition to unite in the proportion of three to one by Mr. Dalton’s theory, I apprehend he might consider the neutral as consisting of 2 particles potash with 1 acid, the binoxolate as 1 and 1 or 2 and 2, the quadroxolate as 1 and 2 or 2 with 4, in which cases the ratios which I have observed of the acids to each other in these salts would respectively obtain.”

Although Wollaston realized that his results may be considered as particular cases of Dalton’s hypothesis (Dalton, 1808) that the atoms of elements united one to one or by some simple multiple relation, he was puzzled as to why he could form these potassium oxalates (corresponding to KHC_2O_4 , $\text{K}_2\text{C}_2\text{O}_4$, and $\text{KH C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$) but not one with a ratio of 2:3. He thought that for a full understanding of chemical combination of atoms “...we shall find the arithmetical proportion alone will not be sufficient to explain their mutual action. And that we shall be obliged to acquire a geometrical conception of their relative arrangement in all three dimensions of solid extension. For instance, if we suppose that the limit to the approach of particles is the same

in all directions, and hence their virtual extent to be spherical (which is the most simple hypothesis); in this case, when different atoms combine singly there is but one mode of union. If they unite in the proportion of two to one, the two particles will naturally arrange themselves at opposite poles of that to which they unite. If there be three, they might be arranged with regularity at the angles of an equilateral triangle...the equilibrium would be unstable...but when the number...exceeds in the proportion of four to one...the four particles are situated at the angles of four equilateral triangles composing a regular tetrahedron” (Hinde, 1966; Goodman, 1969).

Wollaston believed that “it was impossible in several instances, where only two combinations of the same ingredients are known, to discover which of the compounds is to be regarded a consisting of a pair of single atoms...the decision is purely theoretical and by no means necessary to the formation of a table...for practical cases...I have not been desirous of warping my mind according to an atomic theory...” He therefore proposed to draw up a scale, based on an oxygen standard of 10 and on the most reliable analyses available, which would express the proportions in which the common chemical substances combined. These he called *equivalents*, a term invented by Cavendish in the previous century to express the weights of acids and bases which neutralized each other (Cavendish, 1785). Wollaston extended the use of this term in an unfortunate way for it implied that every chemical has a fixed equivalent, an erroneous conception that persisted until thirty years later Auguste Laurent (1807-1853) discovered that chemical equivalence varies with function (Laurent, 1936), Wollaston remarked that he had selected oxygen as his standard “on account of the important part it plays in determining the affinities of bodies by the different proportions in which it is united to them. Nevertheless, the real measure by which most bodies are compared to each other...is a determinate quantity of carbonate of lime. This is a compound that may be regarded as most distinctly neutral; it is most easy to obtain in a state of uniform purity, most easy to analyze; it is a most convenient measure of the powers of acids, and affords the most distinct expression for the comparative neutralizing powers of alkalis.” For example, Wollaston dealt with the oxides of carbon as follows: “The first question...is by what number are we to express the relative weight of carbonic acid, if oxygen is fixed at 100...a given quantity of oxygen yields exactly an equal measure of carbonic acid by union with carbon, and since the specific gravities of these gases are as 10 to 13.77...the weight of carbon may be justly represented by 7.54...and carbonic acid being the protoxide will be duly represented by 17.54” (Wollaston, 1814).

Using this line of reasoning he used the best available

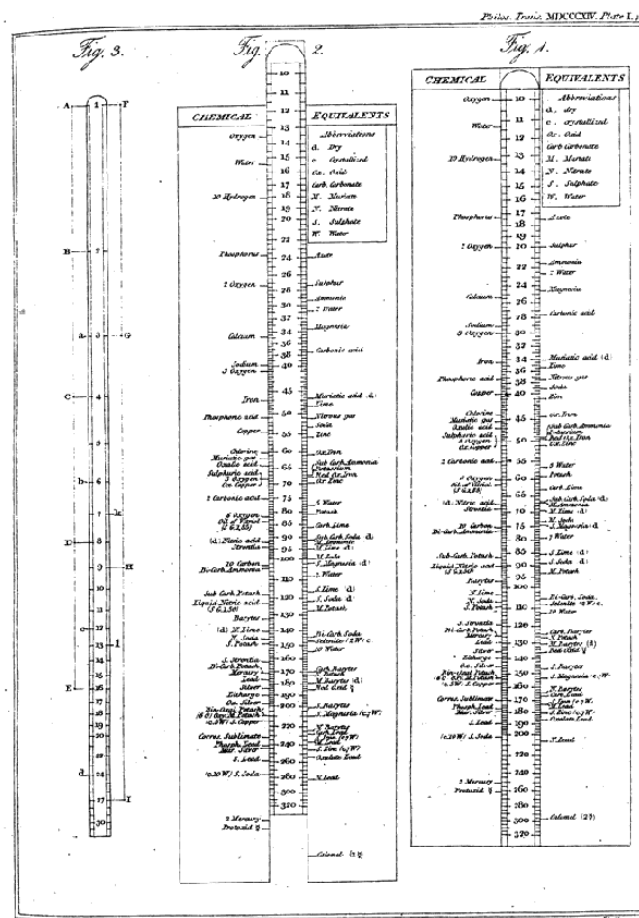


Figure 2. Wollaston's (1814) slide rule, as it appears in the original reference.

analytical information to prepare what he called a *synoptic scale of equivalents*, that is, a list of the equivalent value of the most common compounds (the list contains the values of 58 elements and compounds). He then built a rule (shown in Figure 2), based on a line logarithmically divided from 10 to 320, where he distributed the names and equivalent value of various substances (Wollaston, 1814). This instrument allowed chemists to quickly calculate the “actual weights of the several ingredients...and also the actual quantities of several reagents that may be used, and of the precipitates that would be obtained by each...”, using a mechanical computation instead of lengthy multiplication and division.

It is interesting to note that Wollaston's paper carries a very detailed explanation on how to use his slide rule, because the use of logarithms for performing arithmetical operations was not well-appreciated then: “Those who are acquainted with the doctrine of ratios, and with the use of logarithms as measures of ratios, will understand the principle on which this scale is founded...that the mechanical

addition and subtraction of ratios here performed by juxtaposition, corresponds...to the multiplication and division of the numbers by which those ratios are expressed in common arithmetical notation. To others who are not equally conversant with the nature of logarithms...some further explanation...will be acceptable" (Wollaston, 1814).

Wollaston's chemical slide rule, with or without his numbers, was widely adopted by chemists as a calculating device, irrespective of their views on the atomic theory. For over twenty years it was a standard piece of laboratory equipment and could be bought very cheaply with printed instructions. William Prout (1785-1850) used it to discover what would now be called the empirical formulas of organic compounds. In his manual of laboratory technique, Faraday included a detailed description of Wollaston's instrument, which he said was constantly employed (Goodman, 1969; Faraday, 1827).

Attempts were made before Berzelius to set up tables of atomic weight, which were not very accurate (Berzelius, 1814a). After Gay-Lussac published his work on the combining volumes of gases Berzelius made use of the fact that two volumes of hydrogen combine with one of oxygen and reasoned that two atoms of hydrogen unite with one of oxygen. He therefore halved the value (1.32 in a scale of 10), which Wollaston had given to hydrogen (Hinde, 1966).

In 1822 Wollaston returned to Dalton's theory and tried to prove the existence of atoms through the observation of the planets (Wollaston, 1822). His starting argument was that from the laws of gases we can determine the "degree or rarity" corresponding to different elevations from the earth's surface. Admitting that if the air had been rarified to one percent of the atmospheric pressure, then this occurred at a height of 40 miles. Beyond this limit we were left to conjectures based on the supposed divisibility of matter. If divisibility were infinite so would be the extent of the atmosphere. He argued that the particles of the atmosphere of the Earth were subject to the opposing forces of their mutual repulsion and gravity, then if there were a limit to the divisibility of atmospheric matter the atmosphere would have a sharp limiting height because the expansion of the atmosphere, caused by the repulsive forces between its particles, would be balanced by a definite gravitational attraction acting on finite, indivisible masses. But if matter was endlessly divisible into lighter and lighter particles, the gravitational attraction would be infinitely reduced and the force of repulsion would overcome gravity. Then the atmosphere of the earth would not terminate at a finite height, its expansion no longer checked it would expand freely into celestial space and collect about other planets through gravitational attraction. If observations failed to show the presence of atmospheres on other planets the atoms must exist; if they

were planetary atmospheres other than our own, atoms were fictions. After analyzing the results of many astronomical observations Wollaston concluded "they support the supposition that the earth's atmosphere is of finite extent, limited by the weight of ultimate atoms of definite magnitude no longer divisible by repulsion of their pairs" (Wollaston, 1822).

Many arguments were given against Wollaston's reasoning, for example, by Jean-Baptiste André Dumas (1800-1884), who found no evidence for atoms here or anywhere else. He wished the very word atom would be taken out of chemistry, since it went beyond experience (Dumas, 1836). Thomas Graham (1805-1869) pointed out that another explanation seemed likely (Graham, 1827): since the temperature of the atmosphere decreased with increasing height this cooling alone would condense the atmosphere at a height of about 27.27 miles. Graham believed that the effects of such condensation were visible at the poles where latent heat was supposedly liberated as the aurora borealis, this explaining the phenomenon without mentioning atoms.

3. Electrochemistry

In England, William Nicholson (1753-1815) and Anthony Carlisle (1768-1840) discovered that the electric current could decompose water into its elements while in 1801 Wollaston demonstrated that "the chemical agency of common or frictional electricity is the same as the power excited by chemical means, as in the voltaic pile" (Wollaston, 1801). Wollaston opened his paper with the statement that it is not known if the power from voltaic pile arises from the chemical action of the fluid on the metal or, whether the oxidation itself may not be occasioned by electricity, set in motion by the contact of metals that have different conducting powers.

Wollaston decomposed water using the Leyden jar and found that the difference between a galvanic pile (Volta pile) and the Leyden jar was that the pile had less tension (later called volts), but more quantity (later called current) than that of frictional electricity. Wollaston believed that the decomposition of water depended on the proportioning of electrical charge to a specific quantity of water, and that the discharge of current on the surface of a substance depended on the size of its surface. In 1801 He confirmed Martinus van Marum's (1750-1837) work by demonstrating that copper obtained from a cupric sulfate solution deposited on the wire connected to the negative pole of an electrical machine similarly to that of the pile. The copper coating was found to withstand the operation of burnishing (polishing a surface by friction). In Wollaston's pile, two gold wires, enclosed in capillary tubes, were connected on one end to the friction machine, and other ends were immersed in a solution of cupric sulfate. This arrangement insured that only one point of the metal

was come in contact with the liquid. Wollaston experiments proved clearly that both common and frictional electricity were able to effect a polar chemical decomposition.

Wollaston built several models of batteries. His single cell design consisted of a U-bent copper plate, with a single plate of zinc placed in the center of the bent copper. The zinc plate was prevented from making contact with the copper by pieces or dowels of cork or wood. In design, the copper plate was joined to a horizontal handle for lifting the copper and zinc plates from the activating solution when the battery was not in use. The metal plates and the solution were contained in an earthenware vessel. The multi cell device was constituted of five separate cells in series. The metal plates of each cell were welded to a single overhead bar (replacing the single handle arrangement) that was then mounted to two adjustable ring stand type uprights. This unit formed a trough and was considered an elementary galvanic cell. Wollaston experimented with different sizes of this elementary galvanic cell until he found that one square inch was sufficient to ignite a wire of platinum of 0.003-inch diameter. Operation of the cell left a deposit of copper as a black powder (cupric oxide) on the zinc plate, which had to be constantly scraped off in order to maintain acceptable current amplitude. After a while the Wollaston battery was displaced by improvements of others.

4. Optics

Wollaston's first important work on optics, "A Method of Examining Refractive and Dispersive Powers by Prismatic Reflection" (Wollaston, 1802b), was read to the Royal Society on June 24, 1802. Here he presented a new instrument for measuring the refractive index by total internal reflection, and claimed that his instrument yielded direct results. The method was suggested by consideration of Isaac Newton's (1642-1727) prismatic eyeglass, based on the reflection of light at the inner surface of a dense refracting medium. He found that the variation of the refractive index was a good test for purity and remarked "by placing a varied medium in contact with a prism, all its gradations in density, from greatest to least, become at once the object of mere inspection" (nowadays the refractive index of a solution is a widely used as index of the concentration of a solution). For liquids he made a small cavity in the base of the prism so that only small amounts were required. Wollaston used his apparatus to examine the crystalline lens of the eye, which is known to be more dense in the centre than at its surface. He then measured the limits of refractive power in the crystalline lens of an ox, computed by measuring the refractive density of a dried crystalline of an ox, of which the weight had been taken when fresh, and the quantity of water lost by drying. Wollaston's paper includes a table reporting the refractive index of

64 substances, starting from diamond (2.44, reported by Newton) down to water (1.336) and air (1.00032, reported by Hauksbee). In a following paper (Wollaston, 1802b) he reported his measurements of the double refraction of Iceland spar done with his new refractometer and showed that for different planes of incidence the extraordinary ray was refracted exactly as predicted by Christian Huygens's (1629-1695) wave theory of light (Huygens, 1678).

Wollaston's observations on an impure spectrum led him to conclude that there were only four colors in the solar spectrum: "If the beam of daylight be admitted into a dark room by a crevice 0.05-in broad, and received by the eye at the distance of 10 to 12 feet, through a prism of flint glass, free from veins, held near the eye, the beam is seen to be separated into the four following colors only, red, yellowish green, blue and violet" (Wollaston, 1802a). Between these colors, Wollaston noted dark lines, the Fraunhofer lines. He listed five lines, five of which mark the boundaries of the colors. When Wollaston examined the blue-yellow part of the flame of a candle in the same way, he obtained five images. These hydrocarbon spectral bands were later studied in 1856 by William Swan (1818-1894) at St. Andrews and are now called Swan spectrum (Swan bands are a characteristic of the spectra of carbon stars and of comets).

At the same time he discovered the dark lines in the solar spectrum (later to be known as Fraunhofer lines), which he described as follows: "I cannot conclude these observations on dispersion without remarking that the colors into which a beam of white light is separable by refraction, appear to me to be neither 7, as they usually are seen in the rainbow, nor reducible by any means (that I can find) to 3, as some persons have conceived; but that, by employing a very narrow pencil of light 4 primary diversions of the prismatic spectrum may be seen, with a degree of distinctness that, I believe, has not been described nor observed before" (Wollaston, 1802a).

Wollaston also analyzed the light of a candle and that of an electric spark and observed similar separated images. He closed his paper with the remark that he could explain the difference between the different types of spectrum observed. Half a century later Gustav Robert Kirchhoff (1824-1887) provided an explanation regarding the solar lines was concerned (King, 1954).

Wollaston also experimented with meniscus spectacle glasses employed in ophthalmic practice in the treatment of errors of refraction. He applied his discovery first to the correction of astigmatism of spectacle lenses and then to the camera oscura and camera lucida. He perceived that in order to be free of astigmatism the lens must focus at the same distance lines radial in the field and lines at right angles thereto. This he secured by giving the lens a meniscus



Figure 3. Drawing of Wollaston done with the help of his camera lucida.

form and placing a stop at suitable distance from its concave side. The significance of the distance was that it determined the particular zone of the meniscus through which light passed at a given angle to the lens axis. He first remarked that while the crossed lens of Huygens gave minimum spherical aberration for direct axial pencils and might therefore be suitable for telescope objectives, it gave but mediocre results when used as

a spectacle lens. He suggested that an improvement was at once desirable and simple to effect: "the more nearly an spectacle glass can be made to surround the eye, in the manner of a globular surface, the more nearly will every part of it be at right angles to the line of sight, the more uniform will be the power of its different parts, and the more completely will the indistinctness of lateral objects be avoided". His aim was to make the focal length of the lens for central pencils equal that for oblique peripheral pencils. Hence all positive spectacle lenses "should be more convex on their exterior surface, and concave within" (King, 1954).

In the camera oscura Wollaston placed the lens between the stop and the focal plane, that is, behind the stop. The locus of all image points in the field of Wollaston's lens, which he called periscopic, was not a plane but a surface concave to the lens. At small apertures, the definition was good enough for early photographic cameras, and this simple meniscus is still made by the millions for cheap cameras. Here, a meniscus lens, with concave surface facing the object, can be corrected for astigmatism by placing a stop at a suitable distance in front of the lens. For this particular position the astigmatic difference is zero and the image falls on the József Petzval (1807-1891) surface (When an optical system is well corrected for astigmatism, tangential and sagittal images coincide on the lens curvature surface also called Petzval surface).

In the same paper Wollaston applied the idea of nearly normal refraction to the design of a periscopic simple microscope, or wide-angle magnifier. This is the well-known pair of plano-convex lenses arranged with their plane surfaces in contact but stopped down by placing a small aperture between them (King, 1954).

In 1807 Wollaston described his camera lucida, a quad-

rilateral glass prism, which by two total internal reflections sent horizontal rays from an object vertically upward into the eye viewing above the prism. It consisted of an extendible telescopic tube in three pieces, with 45° prism and sighting lens, which enabled artists to draw outlines in correct perspective. The camera lucida caught on in popularity quickly since no darkroom was needed. The paper was laid flat on the drawing board and the artist would look through a lens containing the prism, so that he could see both the paper and a faint image of the subject to be drawn. He would then fill in the image. The device was secured to the drawing table for stability.

In 1809 Wollaston described his newly invented reflective goniometer (Wollaston, 1809b), which allowed a far greater accuracy in the measurement of crystals. He explained that the modifications of tetrahedrons, of cubes, and other regular solids could be determined with utmost precision with the aid of geometry. Unfortunately, the instruments then available for measuring the angles of crystals did not have the same accuracy, because the radius of contact with the surface was necessarily very short. His apparatus was based on the idea that if the surface of the crystal is sufficiently smooth to reflect a distant image of distant objects, then the position of faces only 0.02 in breadth could be determined with as much precision as those of any larger crystals. In other words, the ray of light reflected from the surface is employed as radius instead of the surface itself. The instrument he designed consisted of a circle graduated on its edge and mounted on a horizontal axle supported by an upright pillar. The crystal was attached with wax to a small leveling device joined to the axle. An object was viewed by reflection on one face of the crystal and then the crystal was rotated until the same object appeared in the adjacent face. The angle through which the graduated circle had moved was read. This procedure gave the angle of the crystal to the nearest five minutes. Wollaston's paper includes a very clear three dimensional view of his apparatus. The modern goniometer is the result of extensive refinements of Wollaston's original design.

In 1800, Wollaston experienced a temporary partial blindness in both eyes after he had been involved in a period of strenuous exercise: "I suddenly found that I could see but half the face of a man whom I met, and it was the same with respect to every object I looked at..." In 1824 the effect caused him to enquire whether others had had similar experiences, and to study the few printed references to this phenomenon related to binocular vision. In the eighteenth century it had been debated whether the faculty of combined two images was inherited or acquired. Wollaston was led to adopt the correct arrangement of semi-decussation of the optic nerves, a disease in which there is a loss of sight in

symmetrical parts of the eye. He wrote a paper in which he described his theory of the phenomenon, a theory now generally accepted (Wollaston, 1824).

5. Urinary calculi

The composition of urinary stones and calculi occupied scientists for many years. In 1776 Karl Wilhem Scheele (1742-1786) discovered that the main component of a bladder stone was a substance that was slightly soluble in water and that the diluted solution colored litmus paper red. The matter melted in alkali and formed a precipitate in acid solution, which dissolved in a hot nitric acid leaving a residue, which after evaporation turned a pinkish crimson. Upon heating, and depending on the temperature, it smelled like prussic acid (HCN), ammonia, or something like burning horn. Scheele named the substance *lithic acid*; subsequently others changed the name to *uric acid*. Scheele's results are important because they established that uric acid was a normal constituent of human urine and that when cold it produced brick-red sediment. Thus uric acid became the first metabolite to be identified in human urine, twenty years before Fourcroy and Vauquelin isolated urea in 1799 (Fourcroy and Vauquelin, 1799ab). Since most stones contained uric acid Scheele reached the wrong conclusion that uric acid was the only constituent.

In 1789 Fourcroy published his first results on the chemistry of biliary stones (Fourcroy, 1789) and that uric acid was rich in carbon and nitrogen but poor in oxygen and hydrogen. According to Fourcroy urinary stones contained uric acids and other substances such as calcium phosphate and magnesium ammonium phosphate; in addition, human renal and bladder stones had a similar composition (Fourcroy, 1793).

In 1800 and 1802 Fourcroy and Vauquelin published two important memoirs on the composition of urinary calculi (Fourcroy and Vauquelin, 1800, 1802), obtained after analyzing over 600 calculi. In these memoirs they changed the name lithic acid to *acide urique* (uric acid). According to their results there were twelve main species of calculi, consisting of the following substances or mixtures of them: uric acid, urate of ammonia, calcium phosphate, magnesium ammonium phosphate, calcium oxalate, and animal matter (gelatin). Uric acid was the commonest constituent. To explain the presence of calcium oxalate they proposed that oxalic acid was normally made somewhere within the walls of the urinary tract, and that it reacted with urine to form microscopic crystals of calcium oxalate. These crystals were usually very small and most of them were excreted as such. Nevertheless, some of them would become nucleation centers for calculi upon which other urinary salts were then deposited (An assumption known today to be true) (Richet, 1995).

Fourcroy and Vauquelin were surprised by the fact that phosphorus was present only as phosphate, in opposition to their findings on other substances such as living tissues, bone, and pollen. These findings may be considered the first indication that other chemical forms of phosphorus may have physiological functions. They also determined that the magnesium present came from the large amounts of it contained in cereals.

Wollaston was one of those who helped to unravel the origin of urinary stones. In 1797 he published a paper (Wollaston, 1798) in which he gave an analysis of gouty concretions and described four new urinary calculi. Until then in England Scheele's lithic acid had made little impression and calculi were first considered to be a sort of chalk and then a material similar to calcium phosphate. To illuminate the etiological origin of urinary stones Wollaston also used precise chemical techniques. He showed that lithic acid was actually a neutral compound consisting of the acid and sodium hydroxide. Upon distillation of the chalk stone lithic acid decomposed yielding a fetid alkaline liquor, a heavy fetid oil, spongy coal, and ammonia, the usual products of animal (organic) substances. He then proceeded to study and analyze four new calculi: (a) Fusible calculi, which he obtained by heating calculi with a blow pipe; instead of burning completely it left a large solid phase, composed of sparkling clear crystals having the form of short triliteral prisms. Wollaston, who was an expert crystallographer, identified the crystals in the deposit to be magnesium and ammonium phosphate, for he could reproduce them by adding ammonia to fresh urine or to a solution of phosphoric acid and magnesium. He had found that, in contrast to magnesium ammonium phosphate, the isolated two salts, ammonium phosphate and magnesium phosphate, could not be melted down; (b) the next stone he analyzed was mulberry calculi, so called because its shape bears a distant resemblance to that fruit. Wollaston believed that the color of the stones was due to small amounts of blood included within them. The stones were found to be composed of an organic acid, oxalic, which is destroyed by combustion leaving a small calcium deposit. Wollaston suspected that oxalic acid came from the vegetable content of the diet; (c) The third calculus he analyzed was the ones, which usually form in the prostate gland but not in the bladder. This he found to be composed of pure, or almost pure calcium phosphate, tinted with the secretions of the prostate gland; (d) the last variety of stones investigated were those originating from the calcification of tissues such as arteries and the valves of the heart. These appeared to be similar to earth of bone, and for this reason he named them bone earth calculi.

To these four calculi Wollaston added, in 1819, a cystine oxide stone. He had observed that this was a nitrogen-con-

taining organic substance that was macro and microscopically and chemically different from uric acid. It was the first amino acid (cystine) to be identified. Soon after, Alexandre Marcet (1770-1822) observed the familiar occurrence of cystine stones. Marcet dedicated his book (Marcet, 1819) to Wollaston with these words: "The chemical history of bodies which form the subject of the following essay, being little more than a sketch of your own discoveries in a department of science in which our knowledge was previously exceedingly imperfect, it is natural I should wish my work to appear under your auspices. If I have ventured to do this without asking your consent it is because I entertained doubts whether you might have scrupled to patronize a work in which your name occurs on almost every page." ■

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